Heat Machines and Quantum Systems: Towards the Third Law

Thesis submitted for the degree of "Doctor of Philosophy"

by

Yair Rezek

Submitted to the senate of the Hebrew University of Jerusalem

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> ...Democritus says that [the soul] is hot, a sort of fire; for while there are infinitely many shapes, i.e. atoms, he says that the spherical ones compose fire and the soul ... because such shapes can most easily penetrate through everything and move the others, being themselves in motion.

- Aristotle, *De Anima* (4th century BCE), showing that Democritus (5th century BCE) already understood heat as molecular (atomic) motion.

> The theory of thermodynamics is today, ca. 100 years after its modern formulation, a basic concept of physics. Its application makes the description and implementation of all sorts of physical and technical processes feasible. Nevertheless, the derivation of basic principles of thermodynamics like, e.g., the famous second law, from more fundamental theories remains an intensively disputed problem until these days. Almost all approaches in that direction are based on classical Newtonian physics. Most of them require additional postulates like the ergodic hypothesis, the ”a priori postulate”, or the ”Stosszahlansatz” which are themselves not part of the Newtonian theory. Furthermore, it is today widely accepted that thermodynamic systems like gases or solids essentially obey quantum rather than Newtonian laws. This recently motivated new attempts to base thermodynamics directly on quantum mechanics.

- Jochen Gemmer (21st century) [1], arguing for quantum thermodynamics.

Abstract

The laws of thermodynamics are generally believed to emerge from the underlying microscopic mechanics. Notable progress has been made in establishing this emergence under classical conditions. The understanding of thermodynamics within deeply-quantum contexts is still lacking, however. The emergence of the third law of thermodynamics is especially problematic. In this thesis, we aim to further the understanding of quantum thermodynamics by considering the dynamic emergence of the laws of thermodynamics in specific models and systems. We focus in particular on the analysis of the cooling rate by a refrigerator using a medium of quantum harmonic oscillators, and on the analysis of cooling in spin systems.

After a brief review of quantum thermodynamics, we argue that in a quantum context the classical formulation of the third law known as the "unattainability principle", which states that it is impossible to cool a system to the absolute zero in a finite number of physical operations, leads to specific implications in regards to the cooling rate. These are in excess of the bounds set on the cooling by the second law of thermodynamics.

We then turn to discussing and analyzing in detail a specific quantum refrigerator, consisting of a quantum analog of the classical Otto cycle. Instead of classical particles in a piston, the working medium is made up of particles in an harmonic (possibly repelling) potential. Contact with thermal heat baths is modeled through Lindblad (completely positive) evolution, in accordance with the theory of open quantum systems. We demonstrate that in the limit cycle the medium is always in a general coherent state, and find the expressions

for its von Neumann and Shannon entropies. We identify a new invariant of the motion, which is related to the Casimir of the relevant Lie algebra.

A thermodynamic analysis of the refrigerator shows that in the quasistatic limit (infinitely slow change of the external controls) the limit cycle achieves the best possible asymptotic behavior for the cooling per cycle, as limited by the second law of thermodynamics. We derive explicit expressions for the cycle's efficiency, cooling per cycle, and entropy generation. We show that the cooling rate is maximized when the oscillator's energy gap is proportional to the energy scale of the cold bath's temperature. Then the cooling rate is limited in accordance with our general discussion.

We find that attempting to move fast, beyond the quasistatic limit, generally leads to quantum friction that hinders the cooling. We discuss quantum friction in this system and in general, and argue that it will generically lead to frictional losses in any refrigeration scheme.

We show, however, that there exist "frictionless" cycles that can achieve the quasistatic cooling per cycle in finite time. We find a simple one directly, and through a more elaborate argument explicitly find the fastest one. Allowing for repelling harmonic potentials, we show that this optimal solution reaches a cooling rate that asymptotically drops with temperature close to the limit allowed by the unattainability principle and the second law.

In the course of this study, we also for the first time establish a minimum time for transitioning between two thermal states. This time is shorter the more energy resources are available, and explodes as the final temperature approaches zero.

Turning to spin systems, we review results obtained for a two-spin Otto cycle and argue that the presence of a minimal energy gap in that case prevented cooling to absolute zero.

We analyze cooling more generally based on the process of "algorithmic cooling". We review previous results that show that using this algorithm it is impossible to set the probability of ground-state for a register of spins below some bound. We generalize these results, arguing that this implies that in any sensible refrigeration scheme it is impossible to cool a finite quantum system beyond a certain minimal (non-zero) temperature. This

temperature approaches zero in the macroscopic limit.

Our results therefore indicate that in the quantum domain the laws of thermodynamics are subtly different. The third law or unattainability principle, while still valid, can be improved upon by providing bounds on the asymptotic behavior of rates or a minimal temperature above zero. These bounds take into account limitations beyond just a ”finite number of operations”, including finite energy gaps, energy resources, and the finite size of the refrigerator and heat baths.

Contents

Chapter 1

Introduction

Thermodynamics is formally an axiomatic theory concerning the dynamics of "heat". But if it is to fit with our mechanistic understanding of the world, the laws of thermodynamics must emerge from the laws of the underlying mechanics and thus "heat" and other thermodynamic terms must be filled with physical content. Traditionally, the laws of thermodynamics are seen as statistical laws emerging from classical mechanics under certain (in practice, inviolate) assumptions. Heat, specifically, is seen as a type of energy.

The understanding of thermodynamics in a quantum context is less clear. In this thesis I suggest that thermodynamics should be explored from the point of view of examining the dynamics of the energy of an open quantum system. This perspective leads to a simple definition of the first law of thermodynamics (the division into work and heat) for time-dependent open systems, and to a natural definition of entropy even far from thermal equilibrium. The second law is maintained universally within this scheme. The validity of the third law, however, is not trivially evident from these definitions. In this thesis I explore its validity in specific models. Focusing on the quantum analog of the third law, I examine the limitations on cooling towards the absolute zero. I suggest that the Third Law of Quantum Mechanics is that cooling finite systems, using finite resources, is restricted to a maximal cooling rate and to a minimum temperature.

The work is divided into sections as follows. In Chapter 2 I discuss the general theoretical background needed to understand the work. I discuss classical thermodynamics and in particular the unattainability principle and the Otto cycle. I discuss the theory of quantum open systems, and the Markovian axiomatic approach to it that I use in this work. I briefly present the standard approach in quantum thermodynamics of time-dependent systems. I then argue that within a quantum context, the unattainability principle implies specific bounds on the asymptotic behavior of the cooling rate at low temperatures.

Chapter 3 is the main body of my work. In it I discuss refrigeration using a particular model, the harmonic-oscillator Otto cycle. I provide a thermodynamic analysis of the refrigerator's operation, and investigate its performance near the absolute zero. My main result is a minimal transition time between two thermal states, and therefore a limit on the possible cooling rate. The cooling rate goes to infinity as the allowed energy resources do, however. From these results, I draw more general insights relating to quantum friction.

Chapter 4 concerns spin systems. Citing previous work, I explain why in a two-spin Otto cycle it is impossible to cool below a finite minimum temperature. I explain the process of algorithmic cooling, and show that it implies that using a finite refrigerator it is impossible to cool a finite system to below a minimal temperature.

Finally, I offer my conclusions in Chapter 5. I suggest scaling laws limiting the cooling rate and minimal temperature that should apply under various limitations, such as using a finite bath, limited energy resources, and so on.

Chapter 2

Theoretical Tools

2.1 Open Quantum Systems

The standard formalism of (non-relativistic) quantum mechanics considers a *closed* quantum system, that does not interact with its environment. The system may be time-independent or, more generally, it can be *time-dependent*. This represents being affected by the environment, but solely by the (semi-)classical effect of an external field. Realistically, however, every physical system is at least somewhat *open*, interacting with the environment in more subtle ways. The treatment of quantum open systems is therefore of fundamental importance, and leads to effects such as decoherence and applications such as stochastic Schrödinger equations [2].

The fundamental idea of the theory of open quantum systems is that an open system can be seen as being a part of a larger, "extended", closed system. One can then derive the properties and dynamics of an open quantum system from the well-understood properties of a closed system.

2.1.1 The Extended System

Consider an extended system, a closed quantum system with some Hilbert space $\mathscr{H}$. This space can be divided into subspaces, so that the extended space is a tensor product of the subspaces. For the purposes of this work, we will divide the total Hilbert space into an open system (S) of interest, and consider the rest to be its environment (B). The extended Hilbert space is hence

$$\mathscr{H}_{tot} = \mathscr{H}_S \otimes \mathscr{H}_B \, . \tag{2.1}$$

The state of a quantum system is often described by a state vector $|\Psi\rangle$ in Hilbert space. More generally, however, it is a statistical mixture of pure states, represented by a density matrix or operator

$$\hat{\rho} = \sum_j p_j |\Psi_j\rangle\langle\Psi_j| \, , \tag{2.2}$$

where the frequencies $p_j \geq 0$ are the normalized $\sum_j p_j = 1$ probabilities of finding the system in the pure state $|\Psi_j\rangle$. The density operator $\hat{\rho}$ is an Hermitian ($\hat{\rho}^\dagger = \hat{\rho}$; assuring Real eigenvalues), positive ($x^\dagger \hat{\rho} x \geq 0$; which assures non-negative eigenvalues), trace-1 ($\mathrm{tr}\left(\hat{\rho}\right) = 1$; which assures normalized probability distributions) operator. The expectation value of any observable $\hat{\mathrm{O}}$ becomes a statistical mixture of the possible pure-state expectation values,

$$\langle\hat{\mathrm{O}}\rangle = \sum_j p_j \langle\Psi_j|\hat{\mathrm{O}}|\Psi_j\rangle = \mathrm{tr}\left(\hat{\rho}\hat{\mathrm{O}}\right) \, . \tag{2.3}$$

The state of each subsystem can be derived by taking the *partial trace* of the extended state. In matrix form, this is equivalent to summing over only the degrees of freedom (dimensions) of the other subsystems. The state of the open system is hence the *reduced state*

$$\hat{\rho}_S = \mathrm{tr}_B(\hat{\rho}) \, . \tag{2.4}$$

The dynamics of the extended system's state are determined by the Liouville-von

Neumann equation

$$\frac{d}{dt}\hat{\rho} = -\frac{i}{\hbar}\left[\hat{\mathrm{H}}_{tot}, \hat{\rho}\right] \equiv \mathscr{L}_{tot}\left[\hat{\rho}\right] \ , \tag{2.5}$$

where

$$\hat{\mathrm{H}}_{tot} = \hat{\mathrm{H}}_S + \hat{\mathrm{H}}_B + \hat{\mathrm{H}}_{SB} \ . \tag{2.6}$$

Here $\hat{\mathrm{H}}_{tot}$ is the Hamiltonian of the extended system, an operator that acts on the extended Hilbert space $\mathscr{H}_{tot}$. $\hat{\mathrm{H}}_S$ is the Hamiltonian of the open system, defined on $\mathscr{H}_S$, while $\hat{\mathrm{H}}_B$ is the Hamiltonian of the environment, defined on $\mathscr{H}_B$. $\hat{\mathrm{H}}_{SB}$ is the interaction of the system with the environment, operating again in the extended Hilbert space $\mathscr{H}_{tot}$. $\mathscr{L}_{tot}$ is the so-called Liouvillian, that defines how to advance the system in time.

We can formally write down the dynamics of the open system from the extended Liouville equation (2.5) and the definition of the reduced state (2.4)

$$\frac{d}{dt}\hat{\rho}_S = -\frac{i}{\hbar}\mathrm{tr}_B\left(\hat{\mathrm{H}}_{tot}, \hat{\rho}\right) \ . \tag{2.7}$$

2.1.2 Quantum Dynamical Semigroups

Solving the dynamics of the quantum open system using equation (2.7), however, requires solving the dynamics of the extended system. As the environment is typically very large, this is often not practical. Approximations must be used to derive more serviceable equations. Perhaps the most natural is the Markovian approximation. Assuming the environment is so stable that it is hardly changed by its interaction with the system, the dynamics of the open system should depend only on the momentary state of the system. The environment is reduced to serving as a mere constant background - typically, a heat bath - to the system's evolution.

Mathematically, we are looking for a *dynamical map* $\Lambda(t)$ that will determine the evolution of the open system

$$\rho_S(t) = \Lambda(t)\rho_S(0) \ . \tag{2.8}$$

But not all dynamical maps would do. We can make three demands, motivated by physical requirements [3, 4].

- **Markovian** First, we demand that the dynamics will be Markovian. This implies

$$\Lambda(t_1+t_2)=\Lambda(t_2)\Lambda(t_1)\ , \tag{2.9}$$

  which characterizes the map as a semigroup (not a full group, as it need not include an inverse Λ^{-1} so that $\Lambda(t)\Lambda(t)^{-1}=1$).

- **Complete Positivity** We also need to take into account the fact that the open system is part of an extended system. The extended system's state must always be positive, and its dynamics maintains its positivity. We therefore demand that the map will be *completely positive*, i.e. that it will preserve the positivity of the extended state.

- **Trace Preserving** The state must also always be a trace-1 operator, so the dynamical map must maintain the trace.

$$\mathrm{tr}_S\left(\Lambda(t)\rho_S(0)\right)=\mathrm{tr}_S\left(\rho_S(0)\right) \tag{2.10}$$

In short, we are looking for a completely positive dynamical semigroup. Any such quantum semigroup can be generated by taking the exponential of a generator $\mathscr{L}$ so that

$$\Lambda(t)=e^{\mathscr{L}t} \tag{2.11}$$

and the dynamics obey the differential equation

$$\frac{d}{dt}\rho_S(t)=\mathscr{L}\rho_S(t)\ . \tag{2.12}$$

2.1.3 Lindblad's Form

In 1976 Lindblad, Gorini and Kossakowsi proved that the generator of a completely positive quantum dynamical semigroup must take a general form [5, 6], which has become known as the *Lindblad form*. It can be written as

$$\frac{d}{dt}\rho_S(t) = -i[\hat{\mathrm{H}}_S, \hat{\rho}_S] + \sum_i \gamma_i \left(A_i \hat{\rho}_s \hat{\mathrm{A}}_i^\dagger - \frac{1}{2}\{A_i^\dagger A_i, \rho_S\} \right) \tag{2.13}$$

$$\equiv \mathscr{L}_S \hat{\rho}_S + \mathscr{L}_D \hat{\rho}_S \, . \tag{2.14}$$

Here $\mathscr{L}_S$ induces the standard unitary evolution that we would have expected from the system's Hamiltonian $\hat{\mathrm{H}}_S$. $\mathscr{L}_D$ represents the effect of the environment. It can generally induce non-unitary, dissipative dynamics (hence the "D"). The sum is on operators $\hat{\mathrm{A}}_i$ that operate on the system's Hilbert space $\mathscr{H}_S$, and are sometimes called Lindblad operators. The factors γ_i are rate constants (having dimensions of inverse time if A_i are dimensionless), and are always positive.

The dynamics of any observable can be determined from that of the state. The expectation value of any observable of the open system is

$$\left\langle \hat{\mathrm{O}}(t) \right\rangle = \mathrm{tr}_S \left(\hat{\mathrm{O}}(t) \right) \, . \tag{2.15}$$

Taking into account Lindbdlad's form (eq. 2.14), this implies

$$\frac{d}{dt}\hat{\mathrm{O}}(t) = \frac{i}{\hbar}\left[\hat{\mathrm{H}}_S(t), \hat{\mathrm{O}}(t)\right] + \sum_i \gamma_i \left(A_i \hat{\mathrm{O}} \hat{\mathrm{A}}_i^\dagger - \frac{1}{2}\{A_i^\dagger A_i, O\} \right) + \frac{\partial}{\partial t}\hat{\mathrm{O}}(t) \tag{2.16}$$

$$\equiv \mathscr{L}_S(\hat{\mathrm{O}}(t)) + \mathscr{L}_D(O(t)) + \frac{\partial}{\partial t}\hat{\mathrm{O}}(t) \, . \tag{2.17}$$

This will be the master equation that I will use throughout this work.

Lindblad's form is a very powerful analytical tool as it allows us to explore the behavior of open quantum systems without needing to worry about the details of the environment.

Indeed, different environment can induce the same Markovian dynamics, the same Lindblad form. There are microscopic derivations that show that Lindblad's form is indeed a good approximation under often-reasonable assumptions [2, 3, 7], and in particular that Lindblad forms that induce thermalization are reasonable. We will from now on therefore make use of Lindblad's form in this way, and forgo a detailed consideration of the microscopic details of the environment and interaction.

The importance of Linblad's form our perspective is that it allow us to ignore the details about how thermalization occurs in practice. Environments often lead to thermalization in a Markovian manner following Lindblad's form. To treat thermalization, we can therefore simply choose Lindblad operators and rates that will induce it. Physical 'thermalization' processes should approach this ideal form.

2.2 Classical Thermodynamics

The first law of thermodynamics is often referred to as the "conservation of energy", but it actually says more than that as it divides changes in energy into two types, work and heat.

$$dE = \delta W + \delta Q \tag{2.18}$$

where E is the energy of the system. The change in work δW and heat δQ is an imperfect differential δ, signifying that it is a function of the path (the thermodynamic process). Both work W and heat Q changes are induced by the environment. The key difference between them is that heat is also featured in the *second* law of thermodynamics, the demand that entropy always increase. Summing over all parts i of the extended system, we can phrase it as

$$\Delta S \geq \sum_i \frac{dQ_i}{T_i} \geq 0\,. \tag{2.19}$$

From the *axiomatic* point of view, then, entropy and the second law are required to understand the division set out in the first law. Heat is defined as that thing that keeps entropy increasing. From the *conceptual* point of view, however, statistical mechanics allowed us to understand work as the change of energy stemming from dynamical changes in the constraints of the system, whereas heat is understood as stemming from energy-exchange in thermal equilibration processes (e.g. [8]). These two distinct meanings of heat, the conceptual and the axiomatic, are merged perfectly in classical mechanics and mechanical statistics. We would suggest, below, that the situation is less clear in the quantum case.

The third law of thermodynamics was first defined by Nernst [9, 10], who developed two main formulations of it, which are equivalent under certain assumptions [10, 11]. The first, which we can term the "entropy principle", states that the entropy of the system approaches zero as its temperature does. We will be more interested in the second, which we can call the "unattainability principle". It states that it is impossible to reach the absolute zero temperature by any finite number of thermodynamic steps. In this work we will be interested in the dynamical ramifications of the third law, that must emerge from the mechanics if it is to hold. Consider some heat Q_c drawn from some system (which we will soon identify with "the cold heat bath") at temperature T_c by some finite-time process. The third law of thermodynamics implies that it must approach zero as the bath's temperature approaches zero [12],

$$dQ_c \xrightarrow[T_c \to 0]{} 0 \,. \tag{2.20}$$

For any specific process, there are two ways in which this can happen. Consider a process that draws a constant amount $dQ_c = \varepsilon$ of heat at each iteration. If the cold bath initially has a high heat capacity, we can repeat the process until its energy (above its ground state) is ε or less. We shall assume that drawing energy lowers the system's temperature, or in other words that the system's ground state is the absolute zero temperature. If its energy is

now precisely ε, then the unattainability principle implies that one more iteration would simply be impossible. This would also be the result of having less than ε remaining, as then it would be impossible to draw ε from the bath at all. The process will simply fail if we try to apply it below a certain minimal temperature T_c, or in other words it is impossible to cool the cold bath to below a certain minimal temperature in this method. Alternatively, the cooling may decrease gradually, so that $dQ_c = 0$ is reached continuously. In this case there is no contradiction with the third law, as each iteration may draw less than the energy currently available in the cold bath, leaving it in a finite temperature.

The third law therefore implies that for any particular finite-time process that draws heat from some "cold bath", the cooling per iteration should decrease gradually to zero or else the process should stop cooling the cold bath at all at some minimal temperature. We will see both types of effects in the thesis.

2.2.1 Refrigeration Cycles

Thermodynamic cycles are a staple of the theory of thermodynamics. They paradigmatically consist of pistons of ideal gas, at a certain volume and pressure, that are brought into contact with various heat baths at temperatures T_i. Each type of cycle is characterized by the manner in which the volume or pressure is changed as the piston is brought into contact, or isolated, from various baths. A cycle that will be important for our analysis is the Otto cycle. It is a four-stroke cycle, consisting of two "adiabatic" steps done without contact with a heat bath, and two "isochoric" branches done at constant volume (see figure 2.1).

- **Hot Isochore** The piston is allowed to thermally equilibrate with a hot bath, while kept at a constant volume.
- **Adiabatic Expansion** The system is decoupled from the hot bath, and allowed expand.

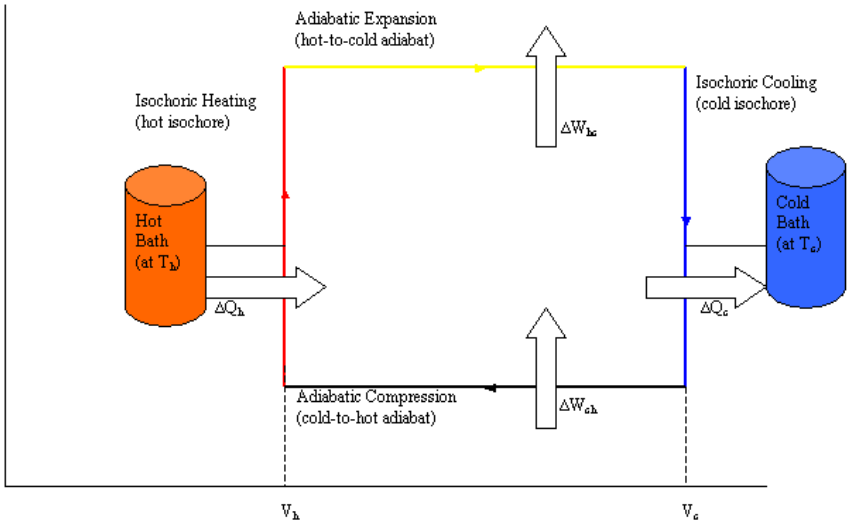


Figure 2.1: The classical Otto cycle, schematically drawn on the entropy-volume plane. The Otto cycle is drawn as an engine, as it is typically considered. In this mode of operation there is heat intake ΔQ_h from the hot bath, exhaust ΔQ_c into the cold bath, and net useful work $\Delta W_{hc} - \Delta W_{ch}$ is produced. The same Otto cycle can, however, be made to work as a refrigerator with the right choice of parameters.

- **Cold Isochore** The system is allowed to equilibrate with a cold bath, while kept at the expanded volume.

- **Adiabatic Compression** The volume of the piston is decreased back to its initial value, after it is isolated from the cold bath again.

Operating in this manner, the gas in the piston will soon approach a *limit cycle*, achieving a state (pressure, temperature, and so on) depending on the parameters of the cycle (the hot bath's temperature, and so on) rather than on its initial state. The properties of a thermodynamic cycle are the properties of its limit cycle.

The classical Otto cycle waits for full thermalization in both isochores, which in theory takes infinitely long time. In finite-time thermodynamics, the gas is allowed to equilibrate partially, for some limited time, before the piston is removed from the heat bath and the adiabatic stroke commences.

We will be interested in refrigeration cycles. The second law of thermodynamics imposes limits on the cooling achievable in any refrigeration limit cycle [12]. Consider some refrigeration cycle operating between two heat baths, a "cold" and "hot" one. Since at each start of the cycle the refrigerator's entropy returns to its previous value, its entropy change from the previous cycle is zero. The entropy of the baths, however, may change. The second law requires that

$$\Delta S = -\frac{Q_c}{T_c} + \frac{Q_h}{T_h} > 0 \,, \tag{2.21}$$

where the signs have been chosen to represent drawing heat ($Q_c > 0$) from the cold bath, and putting it ($Q_h > 0$) in the hot one. Let us now consider lowering the cold bath's temperature T_c towards zero, keeping all other aspects of the cycle (such as the hot bath's temperature) constant. I shall assume that the heat exchange with the hot bath is bounded $Q_h \leq Q_{max}$. The lowered temperature will create a singularity, breaking the second law, unless the cooling per cycle Q_c decreases at least as fast as the temperature. Assuming that Q_c is analytical, to first significant order we must require

$$Q_c \propto T_c^{\delta} \,, \tag{2.22}$$

with $\delta \geq 1$.

Consider now the cooling *rate*, which is the cooling per unit time. For a refrigeration cycle, the average cooling rate is the cooling per cycle divided by the cycle's time $R = Q_c/\tau$. We have already established that the second law limits Q_c. As long as τ does not approach zero as the temperature is lowered, this implies also that $R \to 0$ at this limit. The unattainability principle implies that the integral of the cooling rate $\Delta Q = \int_0^t R(t')dt'$ must always be smaller than the heat capacity of the bath (for any bath, and any cooling method). It is not clear what this implies for the cooling rate in classical thermodynamics, which essentially has no restriction on the bath. We will argue below that within quantum

mechanics this requirement has much clearer and explicit repercussions.

Finally, consider the efficiency of cooling. This is measured by a Coefficient of Performance (COP), which is the amount cooled Q_c divided by the work intake W necessary to perform the cycle

$$\mathrm{COP} \equiv \frac{Q_c}{W} \,. \tag{2.23}$$

Much like an engine's efficiency, the COP for any process between two baths with $T_h > T_c$ is limited by the Carnot limit $\mathrm{COP} \leq \frac{1}{\frac{T_h}{T_c}-1}$, where the equality is obtained if the process is reversible. The COP of an Otto cycle is

$$\mathrm{COP} = \frac{1}{(\frac{V_h}{V_c})^{(\gamma-1)}-1} \,, \tag{2.24}$$

where V_i is the volume at the hot/cold stroke, and $\gamma = \frac{c_p}{c_v}$ is the heat capacity ratio, which is 2 for a two-dimensional monoatomic ideal gas.

2.3 Quantum Thermodynamics

To consider the thermodynamics of a quantum open system, we need to consider the possible changes to its energy

$$E = \mathrm{tr}(\rho_s \hat{\mathrm{H}}_s) \,. \tag{2.25}$$

The first law of quantum thermodynamics should divide the change of energy into work and heat. Such a division was first suggested, in the context of open quantum systems, by

Alicki [13]. He suggested to partition changes to the energy $E = \mathrm{tr}(\hat{\rho}\hat{H})$ as follows:

$$\dot{Q} = \mathrm{tr}\left(\frac{d\hat{\rho}}{dt}\hat{\mathrm{H}}\right) \tag{2.26}$$

$$\dot{W} = \mathrm{tr}\left(\hat{\rho}\frac{d\hat{\mathrm{H}}}{dt}\right) \tag{2.27}$$

Geva and Kosloff [14–16] rewrote these equations in the Heisenberg picture as

$$\dot{Q} = \langle \mathscr{L}_D(\hat{\mathrm{H}})\rangle \tag{2.28}$$

$$\dot{W} = \langle \frac{\partial \hat{\mathrm{H}}}{\partial t}\rangle \,. \tag{2.29}$$

These are the definitions of work and heat that I will use throughout this work. *Conceptually* they correspond to considering work as the change of energy related to the change of external constraints, changing the Hamiltonian directly, and heat as related to other changes in energy populations as energy is exchanged with the environment.

As noted above, *axiomatically* the meaning of heat lies in its relation to the second law of thermodynamics and therefore to the entropy. In a quantum mechanical context, von Neumann defined the von Neumann entropy of the state

$$S = -\mathrm{tr}\,(\hat{\rho}\log(\rho)) \tag{2.30}$$

in analogy to the Gibbs entropy [17]. Assuming that the entropy change of the environment is related to the definition of heat above via the standard relation $dS = dQ/T$, Alicki was able to show [13] that Lindbladian dynamics (with a time-dependent Hamiltonian) imply positive entropy generation,

$$\sigma = \frac{dS}{dt} + \frac{\dot{Q}_h}{T_h} - \frac{\dot{Q}_c}{T_c} > 0\,, \tag{2.31}$$

where in the above formula I have restricted the general case considered by Alicki to the

case of pouring heat into the hot bath and drawing it from the cold one.

The above formulation of the first law demonstrates that quantum thermodynamics is truly a *dynamical* theory. Whereas classical thermodynamics is concerned with imperfect differentials $đQ$ that take place in an abstract reality removed from physical time, quantum thermodynamics is concerned with time derivatives $\frac{d}{dt}$ and is inherently concerned with physical processes, that take time to complete. Classical thermodynamics, despite its name, is strictly concerned with processes near thermal equilibrium and hence requires quasistatic changes that take infinite time to perform. Quantum thermodynamics extends to processes and states well outside thermal equilibrium, and is thus closer to the field of finite-time (classical) thermodynamics.

2.3.1 Quantum Refrigeration Cycles

Quantum thermodynamic cycles are defined much like the classical ones, as repeated series of operations and processes leading to a limit cycle. Based on the above definitions of work and heat, however, we can divide strokes into two fundamental types.

In an *adiabatic* stroke the system is isolated from any thermal environment. It is evolving under a time-dependent Hamiltonian, but the dissipator $\mathscr{L}_D$ is zero. In this case the change of energy can be attributed to work alone. Note that the von Neumann entropy is invariant under unitary evolution, so that such processes are isentropic $dS = 0$. This corresponds well to classical adiabatic processes, where $dQ = TdS = 0$.

In a *thermalization* stage the system's Hamiltonian remains time-independent, but its environment induces some dissipation $\mathscr{L}_D \neq 0$ which we will assume, for simplicity, is thermalization. The change of energy can then be attributed to heat alone. Note that in this case the von Neumann entropy can change. If we define the temperature as

$$T \equiv \left(\frac{\delta S}{\delta E}\right)^{-1}, \tag{2.32}$$

we can formally write $dE = TdS = \delta Q$. This is in analogy to the classical case, where

$T = \left(\frac{dE}{dS}\right)|_V$, i.e. the derivative where the external constraints (such as the volume V) are kept constant. In both the quantum and classical cases this is an imperfect differential, as the heat and entropy in two different processes can change differently while arriving at the same final energy.

Realistic processes will likely combine both effects, and cycles can be constructed with such strokes. However, from a theoretical standpoint these two types of processes neatly separate the thermodynamic variables and simplify the treatment, requiring time-independent (and hence easier) open systems treatment on the thermalization strokes and standard quantum mechanical approaches for closed systems on the adiabatic ones. This is why the Otto cycle, consisting of only adiabatic and thermalization strokes, is the fundamental thermodynamic cycle for quantum systems.

Finally, I argue that in a quantum context the unattainability principle implies that the cooling rate should drop faster than $R = Q_c/\tau \propto T_c^1$. The limiting scaling can be achieved by the maximal cooling per cycle allowed by the second law, if the cycle's time is independent of temperature. To see that this is in contradiction to the third law, assume that near the absolute zero we can think of the bath as a two-level system, and (without loss of generality) that its ground state energy is zero and it has an energy gap ΔE. For low temperatures ($T_c \to 0$), its energy is approximately $E \approx \exp(-\Delta E/k_B T_c^{(0)})\Delta E$. Then a single cycle operation (taking some fixed time τ) will draw some heat $f(T_c)$ from the bath, defining a new temperature $E = \exp(-\Delta E/k_B T_c^{(1)})\Delta E = \exp(-\Delta E/k_B T_c^{(0)})\Delta E - f(T_c^{(0)})$. If we let the heat intake scale as the maximum allowed by the second law, $f \propto T_c$, then the temperature will drop nearly-exponentially with time, until it will drop so much that another iteration would supposedly bring us to zero (or below); since this is impossible by the unattainability principle, it should simply be impossible to maintain the ideal scaling $Q_c \propto T_c$ below a certain temperature. Indeed, f must scale at least as fast as the exponent in order for there not to be some cut-off minimal temperature. I conclude that for cycles of finite, fixed, time τ the cooling-per-cycle and cooling rate must drop exponentially, or else meet a sharp cut-off at some finite minimum temperature T_c^{min} below which no cooling

would be performed.

The situation is markedly different if the cycle's time changes with the temperature. If it approaches zero at the limit of zero temperature, then the cooling rate becomes infinite and the unattainability principle will be trivially violated. It may, however, change so that it approaches infinity for low temperatures $\tau \to \infty$. In this case completing the last cycle, that brings us to zero energy (and temperature) in violation of the unattainability principle, is impossible in finite time. There is therefore no hindrance to achieving the maximum cooling per cycle, $Q_c \propto T_c$. The cooling rate $R = Q_c/\tau$, however, will necessarily approach zero *faster*. Assuming it is analytic, we can conclude that the third law of quantum thermodynamics implies

$$R \propto T_c^{\delta} \tag{2.33}$$

with $\delta > 1$. Such a scaling can be only achieved, however, if the cycle time goes to infinity at this limit; if it is finite, the scaling must be exponential or, barring that, a minimum temperature T_c^{min} should emerge below which no cooling is possible.

Chapter 3

The Harmonic Oscillator

In this chapter, which is the main part of my work, I want to use a particular model to explore the emergence of thermodynamics from quantum mechanics, and in particular the third law that limits cooling near the absolute zero. The model I will focus on will be the harmonic oscillator, which allows me to develop analytical solutions.

Since I want to explore cooling, I need to look at an open system that is externally operated on so that it functions as a refrigerator. I therefore look at quantum particles that serve as the "working fluid" or gas of the refrigerator. These are kept in a "piston", or some bounding potential, which for simplicity I will take to be a one-dimensional harmonic potential. Thus the system's Hamiltonian is that of an harmonic oscillator

$$\hat{\mathrm{H}} = \frac{1}{2m}\hat{\mathrm{P}}^2 + \frac{1}{2}k(t)\hat{\mathrm{Q}}^2 = \hbar\omega(t)(\hat{\mathrm{a}}^\dagger(t)\hat{\mathrm{a}}(t) + \frac{1}{2}) \,, \tag{3.1}$$

where to increase generality I would also allow a repelling potential that has a negative spring constant ($k < 0$) or, equivalently, imaginary frequency ω.

By changing the frequency and contact with heat baths appropriately, this open system can function as an Otto refrigeration cycle. In this chapter I explain the cycle and its dynamics, and derive some general results. I then focus on infinitely slow (quasistatic) operation, presenting a full thermodynamic analysis of its performance. Moving to finite

but slow rates, I show that the finite speed results in friction. I show that this is generally true for arbitrary speeds, and argue that it signifies a quantum source of friction that is generic and is to be expected in any quantum process.

I then show that there are, however, frictionless cycles in finite time. I determine the fastest one, leading to the fastest possible cooling, and discuss the relation of this result to the third law of thermodynamics.

This chapter summarizes several articles and publications [18–24].

3.1 The Refrigeration Cycle

We are interested in cooling some environment (the "cold bath") using a quantum open system consisting of (one-dimensional) harmonic oscillators. There are many ways in which such a system can be made to cool the bath. In this work I will apply the quantum Otto refrigeration cycle (cf. section 2.3.1). This cycle consists of four stages (see figure 3.1):

- **Hot Thermalization** In this stage the frequency of the oscillator is kept constant at ω_h while it is brought into contact with a hot thermal reservoir. The system equilibrates to the heat bath's temperature at this frequency, setting fixed "initial conditions" for the following cooling steps.

- **Adiabatic Expansion** In this stage the working fluid is isolated thermally from the environment, so it is "adiabatic" in the thermodynamic sense of not exchanging heat. The frequency of the oscillator is decreased[1] to ω_c, leading to a decrease in its energy and a drop in its temperature.

- **Cold Thermalization** In this stage the frequency of the oscillator is held constant as it is brought into contact with the cold heat bath. The working fluid is colder still,

[1] The decrease in frequency can be thought of as "expansion" if volume is thought of as the inverse of the frequency $V = 1/\omega$. This is a valid analogy as increasing the volume then leads to a decrease in the energy, in accordance with classical thermodynamics $dU = -PdV$. See [18] for further discussion.

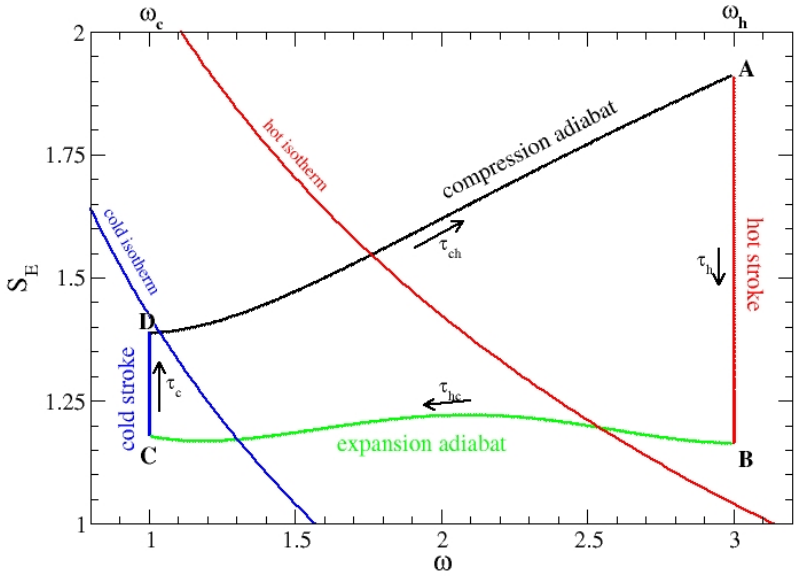


Figure 3.1: A typical quantum Otto refrigeration cycle. The frequency is noted on the x-axis, and the Shannon energy entropy on the y-axis. The cycle operates clockwise, starting at point A at the beginning of the hot thermalization stage and continuing with the four strokes. A finite time is spent on each segment. Isothermals at the bath temperatures are also drawn for comparison. Note that the cycle never reaches full equilibration.

leading it to heat up as it thermalizes, drawing heat from the cold bath. Thus the refrigerator cools the target (the cold bath).

- **Adiabatic Compression** Finally, the system is again decoupled thermally and the frequency of the oscillator brought back up to ω_h. It can now brought into contact with the hot bath again, restarting the cycle.

All four strokes are in finite time, so that thermalization is partial and the change in frequency is not infinitely slow. Nevertheless, as we will show below, the cycle approaches a limit cycle whose performance does not depend on the initial conditions of the working fluid.

We can establish a bound on the cooling per cycle from this description alone.

The cooling per cycle Q_c is the energy change along the cold thermalization branch.

$$Q_c = E_D - E_C = \hbar\omega_c(n_D - n_C) \tag{3.2}$$

where n_i is the expectation value of the population operator $\hat{\mathrm{N}} = \hat{\mathrm{a}}^\dagger\hat{\mathrm{a}}$ at point i on the cycle (see figure 3.1). To bound this quantity, consider that we expect heat intake from the bath, i.e. that we require the energy to increase along the cold thermalization stroke so that $n_D \leq n_{Ceq}$ (where n_{Ceq} is the value at equilibrium with the cold bath). Since the population at point C is always positive, we can obtain a bound by simply setting $n_C = 0$. Then we can write

$$Q_c \leq \hbar\omega_c \frac{1}{e^{\beta_c\hbar\omega_c} - 1} \,. \tag{3.3}$$

Optimizing with respect to ω_c we obtain that Q_c drops with $R_c \equiv \beta_c\hbar\omega_c$, so that $R_c \to 0$ is desirable to keep it maximal. At the limit of $R_c \ll 1$, however, the above formula reduces to

$$Q_C^* < k_B T_c \,. \tag{3.4}$$

We obtain that as $T_c \to 0$, the cooling per cycle Q_c could at most scale as $Q_c \propto T_c^1$. Note that this is precisely the scaling allowed by the second law of thermodynamics (cf. section 2.2.1).

We are particularly interested in the cooling rate $R = Q_c/\tau$, where $\tau = \tau_h + \tau_{hc} + \tau_c + \tau_{ch}$ is the sum of the times allocated to each branch. To take the times into account, however, we must turn to consider the actual dynamics along the different segments.

3.1.1 The Adiabatic Strokes

Along the two adiabatic stages we change the frequency of the oscillator while it is decoupled from the baths, treating it as a closed quantum system. For thermodynamic purposes we are interested in the dynamics of the energy, but deriving its equation of motion shows that this change entangles it with two more quantities: the Lagrangian and the position-momentum correlation. We receive three coupled differential equations of motion

$$\frac{d}{dt}\begin{pmatrix}\hat{\mathrm{H}}\\ \hat{\mathrm{L}}\\ \hat{\mathrm{C}}\end{pmatrix}=\begin{pmatrix}\frac{\dot{\omega}}{\omega} & -\frac{\dot{\omega}}{\omega} & 0\\ -\frac{\dot{\omega}}{\omega} & \frac{\dot{\omega}}{\omega} & -2\\ 0 & 2 & \frac{\dot{\omega}}{\omega}\end{pmatrix}\begin{pmatrix}\hat{\mathrm{H}}\\ \hat{\mathrm{L}}\\ \hat{\mathrm{C}}\end{pmatrix}, \tag{3.5}$$

where we have defined

$$\hat{\mathrm{H}}=\frac{1}{2m}\hat{\mathrm{P}}^2+\frac{1}{2}k(t)\hat{\mathrm{Q}}^2 \tag{3.6}$$

$$\hat{\mathrm{L}}=\frac{1}{2m}\hat{\mathrm{P}}^2-\frac{1}{2}k(t)\hat{\mathrm{Q}}^2 \tag{3.7}$$

$$\hat{\mathrm{C}}=\frac{\omega}{2}\left(\hat{\mathrm{P}}\hat{\mathrm{Q}}+\hat{\mathrm{Q}}\hat{\mathrm{P}}\right). \tag{3.8}$$

We can therefore determine the dynamics of the energy expectation value $H=\langle\hat{\mathrm{H}}\rangle$ if we simultaneously consider the other two expectation values $L=\langle\hat{\mathrm{L}}\rangle$ and $C=\langle\hat{\mathrm{C}}\rangle$.

As these equations of motion are time-dependent, it is impossible to present a general solution. We will instead consider special solutions below.

3.1.2 The Thermalization Strokes

The dynamics on a thermalization stroke are simply those of thermalization (at constant frequency). We can represent thermalization using Lindblad's form (see section 2.1.3). It involves two processes: one increasing the energy by one quant $a^\dagger$ with a rate $k_\uparrow$, and one decreasing it by one quant a with a rate $k_\downarrow$. The two rates must maintain detailed balance

$k_\downarrow/k_\uparrow = e^{-\beta\hbar\omega}$. Taking these rates and Lindblad operators, we are led to the equation of motion for any observable

$$\frac{d}{dt}\hat{\mathrm{O}} = -i[\hat{\mathrm{H}},\hat{\mathrm{O}}] + \frac{\partial}{\partial t}O(t) + k_\downarrow\left(\hat{\mathrm{a}}\hat{\mathrm{O}}\hat{\mathrm{a}}^\dagger - \frac{1}{2}\{\hat{\mathrm{a}}\hat{\mathrm{a}}^\dagger,\hat{\mathrm{O}}\}\right) + k_\uparrow\left(\hat{\mathrm{a}}^\dagger\hat{\mathrm{O}}\hat{\mathrm{a}} - \frac{1}{2}\{\hat{\mathrm{a}}^\dagger\hat{\mathrm{a}},\hat{\mathrm{O}}\}\right) . \quad (3.9)$$

This will lead to thermalization with a constant rate $\Gamma = k_\uparrow - k_\downarrow > 0$, i.e. $H(t) = (H_0 - H_{eq})e^{-\Gamma t} + H_{eq}$. With the correct choice of constants, the correct equilibrium energy $H_{eq} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$ for an oscillator with frequency ω at temperature $T = \frac{1}{k_B\beta}$ can also be achieved.

Applying equation (3.9) to the other two operators of interest $\hat{\mathrm{C}}$ and $\hat{\mathrm{L}}$ results in a similar exponential approach to the appropriate thermal equilibrium values, $L = C = 0$.

3.1.3 General Properties

The state of the working medium in general is not in thermal equilibrium. In order to consider its general state, let us consider the so-called "general coherent state", which is the state of maximum entropy subject to to a set of expectation values $\langle\hat{\mathrm{X}}_j\rangle = \mathrm{tr}\left(\hat{\mathrm{X}}_j\hat{\rho}\right)$:

$$\hat{\rho} = \frac{1}{Z}exp\left(\sum_j \beta_j\hat{\mathrm{X}}_j\right) \quad (3.10)$$

where β_j are Lagrange multipliers. The generalized canonical form of equation (3.10) is useful only if the state can be cast in the canonical form during the entire cycle of the engine, leading to $\beta_j = \beta_j(t)$. This requirement is called canonical invariance [25]. A necessary condition for canonical invariance is that the set of operators $\hat{\mathrm{X}}$ in equation (3.10) is closed under the equations of motion, i.e. it forms a dynamical Lie algebra [26, 27]. If this condition is also sufficient for canonical invariance, then the state of the system can be reconstructed from a small number of quantum observables $\langle\hat{\mathrm{X}}_j\rangle(t)$, which are the thermodynamic observables in the sense that they define the state under the maximum entropy principle.

The condition for canonical invariance on the unitary (adiabatic) part of the evolution in the cycle is as follows. If the Hamiltonian is a linear combination of the operators in the set $\hat{\mathrm{H}}(t) = \sum_m h_m \hat{\mathrm{X}}_m$ and the set forms a closed Lie algebra $[\hat{\mathrm{X}}_j, \hat{\mathrm{X}}_k] = \sum_l C_l^{kj} \hat{\mathrm{X}}_l$, then the set $\hat{\mathrm{X}}$ is closed under evolution [28] and canonical invariance prevails [29]. For the harmonic oscillator, sets such as $\{\hat{\mathrm{H}}, \hat{\mathrm{L}}, \hat{\mathrm{C}}\}$ or $\{\hat{\mathrm{H}}, \hat{\mathrm{a}}, \hat{\mathrm{a}}^\dagger\}$ fulfill these conditions.

On the thermalization stages the set has to be closed also to the operation of the dissipator $\mathscr{L}_D$. This is also fulfilled for the aforementioned sets for an harmonic oscillator. This is only a necessary condition, however, and need not be sufficient. Nevertheless, for the harmonic working fluid and the dissipator $\mathscr{L}_D$ defined in equation (3.9) the closure is also sufficient for canonical invariance to take place [19].

Let us suppose that at some point on the cycle the system is in the "general coherent" [30] state

$$\hat{\rho} = \frac{1}{Z} e^{\gamma \hat{\mathrm{a}}} e^{-\beta \hat{\mathrm{H}}} e^{-\gamma^* \hat{.} a^\dagger} \tag{3.11}$$

Note that a thermal state is such a state with $\gamma = 0$. The dynamics maintain this state, and it is therefore also the state at the limit cycle. It therefore follows that this is the state along the limit cycle, regardless of initial conditions. We can therefore constantly assume that, at the limit cycle, the state is always in this general coherent form.

Having an explicit form allows us to determine the entropy of the system. The von Neumann entropy of the state (3.11) turns out to be [22]

$$S_{VN} = \log\left(\sqrt{X - \frac{1}{4}}\right) + \sqrt{X}\,\mathrm{asinh}\left(\frac{\sqrt{X}}{X - \frac{1}{4}}\right), \tag{3.12}$$

where

$$X = \frac{H^2 - L^2 - C^2}{\hbar\omega}. \tag{3.13}$$

Note that the von Neumann entropy should be invariant under unitary evolution[31], and indeed the quantity X is invariant under our equations of motion (equation 3.5). This can be understood on group-theoretic grounds as the invariance of the dynamical Lie algebra's Casimir to group (and, particularly, $\hat{\mathrm{H}}$) operations.

The Shannon energy entropy of the system turns out to be [19]

$$S_E = \frac{1}{\hbar}\omega\left(H+\frac{\hbar\omega}{2}\right)\log\left(\frac{2H+\hbar\omega}{2H-\hbar\omega}\right)-1\left(\frac{2\hbar\omega}{2H-\hbar\omega}\right) . \tag{3.14}$$

We can define a "temperature" that measures how much the energy changes when the energy-entropy does, $T \equiv \frac{\partial H}{\partial S_E}$. The temperature of our system is hence

$$k_B T = \frac{\hbar\omega}{\log\left(-\frac{-4H^2+(\hbar\omega)^2}{(2H-\hbar\omega)^2}\right)} . \tag{3.15}$$

The inverse temperature $1/k_BT$ essentially measures how much the energy spreads (S_E grows) as energy is put into the system. One should note that this is not, in general, the coefficient β in the general coherent state; the coefficient is only equal to the inverse temperature if $\gamma = 0$.

3.1.4 The Quasistatic Cycle

As noted, the equations of motion on an adiabatic segment cannot be solved in general, so we must consider special solutions. A simple - and important - case is the quasistatic cycle, where the frequency is changed infinitely slowly. The harmonic oscillator has an adiabatic conserved quantity $\hat{\mathrm{H}}/\hbar\omega$ [32]. This means that in the "quasistatic limit" of a slow change in frequency $\omega(t)$, this quantity will be conserved. A quasistatic change from ω_i and energy E_i to frequency ω_f will therefore lead to a final energy of $E_f = (\omega_f/\omega_i)E_i$. We can therefore determine the energy at the end of an adiabatic stroke by knowing only its initial energy. We have already established that the dynamics on a thermalization branch is also simple (equation 3.9), so that knowing the initial energy at its beginning we can

similarly determine it at its end. We can therefore let go of the other two expectation values L and C and consider the dynamics of H alone. Demanding that the cycle closes leads us to a single limit cycle, independently of initial conditions.

The cooling performed per such cycle is

$$Q = \frac{(e^{x_h}-1)(e^{x_c}-1)}{e^{x_h+x_c}-1}\hbar\omega_c\left(n_{Ceq}-n_{Heq}\right) \tag{3.16}$$

$$\equiv F(\Gamma_h,\tau_h,\Gamma_c,\tau_c)\cdot G(\beta_c,\omega_c,\beta_h,\omega_h)\ , \tag{3.17}$$

where $x_i = \Gamma_i\tau_i$ are dimensionless measures of the time spent on each thermalization branch, and $n_{H/Ceq}$ is the thermal equilibrium value of the population operator in equilibrium with the hot/cold bath. We can write G and F explicitly as

$$F = \frac{(e^{\Gamma_h\tau_h}-1)(e^{\Gamma_c\tau_c}-1)}{e^{\Gamma_h\tau_h+\Gamma_c\tau_c}-1} \tag{3.18}$$

$$G = \frac{\hbar\omega_c}{2}\left(\coth(\beta_c\hbar\omega_c/2)-\coth(\beta_h\hbar\omega_h/2)\right) \tag{3.19}$$

Note that cooling per cycle Q_c is maximized when $z = \Gamma_c\tau_c = \Gamma_h\tau_h$ is maximized, and when $\mathscr{R}_c \equiv \beta_c\hbar\omega_c$ is minimized. From G one can see that a condition for cooling is that $\mathscr{R}_c < \mathscr{R}_h$, so that $\omega_h/\omega_c > T_h/T_c > 1$. (Working at the opposite inequality will result in an engine-cycle [19].) The cold frequency must hence be smaller than the hot one, which is consistent with our description of the cycle above.

The efficiency of cooling is measured by the Coefficient of Performance (COP), which is the intake of heat from the cold bath across the cycle Q_c, divided by the total amount of work invested to perform it. For the quasistatic cycle, this is

$$\mathrm{COP} = \frac{1}{\frac{\omega_h}{\omega_c}-1} \tag{3.20}$$

Note that the COP is always positive as long as $\omega_h > \omega_c$. Because $\omega_h/\omega_c > T_h/T_c$, the maximum COP is the Carnot limit $1/(T_h/T_c-1)$.

As the quasistatic cycle is closed, the entropy of the cycle is cyclical as well. But the entropy of the universe - of the baths - should increase as we operate the cycle. Summing the heat exchange with the two baths divided by the bath's temperature, we indeed obtain an entropy change that is always positive (regardless of the choice of parameters):

$$\Delta S = \frac{(e^{x_h}-1)(e^{x_c}-1)}{e^{x_h+x_c}-1}\hbar\left(\beta_h\hbar\omega_h - \beta_c\hbar\omega_c\right)\left(n_{Ceq}-n_{Heq}\right) . \tag{3.21}$$

Entropy production is maximized when $z = x_h = x_c$ and when $\mathscr{R}_c \ll 1$ and $\mathscr{R}_h \gg 1$ (or vice versa).

The cooling rate $R = Q/\tau$ for the quasistatic cycle is strictly zero, as each quasistatic adiabatic stroke takes infinite time. Thinking of this limit more physically, however, we can effectively reach it with a slow-enough stroke. Let us assume that the adiabatic strokes take some finite time τ_{adi}, so that $R = Q/(\tau_h + \tau_c + \tau_{adi})$. For simplicity, we will limit ourselves to the case of equally strong heat coupling to both heat baths, $\Gamma = \Gamma_c = \Gamma_h$. The function F/τ is then maximal when $z = x_h = x_c$ and

$$2z + \Gamma\tau_{adi} = \sinh(z) , \tag{3.22}$$

and the function F/τ takes the simple form

$$F/\tau = \Gamma\frac{2e^z}{(1-e^z)^2} . \tag{3.23}$$

In the limit when the time spent on the adiabats τ_{adi} is long, the condition $2z + \Gamma\tau_{adi} = \sinh(z)$ becomes $\Gamma\tau_{adi} \approx 1/2\exp(z)$, and F/τ becomes simply

$$F/\tau = \frac{1}{\tau_{adi}} . \tag{3.24}$$

We expect the time spent on the adiabats to become longer as we reach low temperatures of the cold bath, as a consequence of the third law of thermodynamics preventing us from

cooling to zero temperature. We hence expect this result to be applicable near the zero temperature.

To characterize the behavior of the cooling rate at this limit, then, we need to characterize the behavior of the time τ_{adi}. Since we are at the limit of a slow change of frequency, we must require that $\dot{\omega}/\omega^2 \ll 1$. Let us focus on the adiabatic expansion, which is critical for the cooling, and assume initially (for simplicity) a linear change of frequency $\omega(t) = \omega_0 + \alpha t$. Then the demand for a slow adiabat translates into the demand that $(\omega_h - \omega_c)/(\tau_{exp}\omega_c^2) \ll 1$ so that

$$\tau_{adi} \propto \omega_c^2 \,. \tag{3.25}$$

We can see that this quantity will explode, as expected thermodynamically, if ω_c decreases as T_c does. This can be accomplished by any power of ω, however. Let us relaxes our demand for linear frequency change, and assume that at small temperatures τ_{adi} would scale like some power of the cold frequency ω_c,

$$\tau_{adi} = \alpha \omega_c^{-\delta} \,. \tag{3.26}$$

Since $R = G/\tau_{dai}$, this implies

$$R = \frac{\hbar}{\alpha}\left(\frac{1}{e^{\beta_c\hbar\omega_c}-1} - \frac{1}{e^{\beta_h\hbar\omega_h}-1}\right)\omega_c^{1+\delta} \,. \tag{3.27}$$

This function is maximized when

$$(1+\delta)\left(\frac{1}{e^{\mathscr{R}_c}-1} - \frac{1}{e^{\mathscr{R}_h}-1}\right) - \frac{\mathscr{R}_c e^{\mathscr{R}_c}}{(e^{\mathscr{R}_c}-1)^2} = 0 \,. \tag{3.28}$$

Assuming we don't change the parameters on the hot side of the cycle (which we already know we should set so that $\mathscr{R}_h$ is as high as possible), the maximum cooling rate is obtained

when $\mathscr{R}_c$ is constant.

$$\omega_c^* \propto T_c \tag{3.29}$$

(where ω_c^* is the optimal choice of frequency). This is consistent with our previous observation that ω_c should drop as T_c does, and now we know it should drop linearly to maximize the cooling rate.

We obtained that in the quasistatic limit the maximum cooling rate towards the absolute zero depends on some power of the cold bath's temperature

$$R \propto T_c^{1+\delta} \tag{3.30}$$

with $\delta > 1$. We note that for a linear frequency change specifically we received $R \propto T_c^3$.

The third law of thermodynamics therefore emerges in this quantum mechanical model as a dynamic constraint that increases the time needed to perform each cycle as we drop the temperature, leading to a constraint on the cooling rate above that obtained from the second law (which corresponds to $\delta = 0$, cf. section 2.2.1).

3.2 Quantum Friction

Let us consider a cycle that is nearly at the quasistatic limit. We have so far derived only the thermodynamic results at the exact limit. What are the first-order corrections to the above results? These can be obtained by constructing solutions to the equations of motion (equation (3.5)) that are correct to first order in the equation's parameters measuring the speed the frequency change, $\alpha \equiv \dot{\omega}/\omega$ [19, 20]. The first significant corrections turn out to be dependent on α^2, signifying that it is the speed of the frequency change rather than the direction of change that matters. For reasons that would become readily apparent, we will refer to these corrections as frictional (f) terms.

The cooling per cycle is reduced to $Q = Q_0 + \Delta Q^{(f)}$, where Q_0 is the cooling per cycle at the quasistatic limit (equation (3.16)) and $\Delta Q^{(f)}$ is the correction to the first significant order.

$$\Delta Q_c^{(f)} = -\left(\frac{\alpha}{2\omega_h}\right)^2 \frac{\hbar\omega_c}{2}\coth\left(\beta_h\hbar\omega_c\right) \tag{3.31}$$

This quantity is always negative, so that operating close to the quasistatic limit always lowers the cooling performed per cycle.

The COP is also lowered,

$$\Delta\mathrm{COP}^{(f)} = -\frac{\alpha^2}{4\omega_c\omega_h}\frac{\omega_h^2\coth(\beta_h\hbar\omega_h) + \omega_c^2\coth(\beta_h\hbar\omega_h)}{(\omega_h-\omega_c)^2(\coth(\beta_c\hbar\omega_c) - \coth(\beta_h\hbar\omega_h))}\,. \tag{3.32}$$

The entropy production is increased [19],

$$\Delta S^{(f)} = \frac{1}{8}\left(\left(\frac{\alpha}{\omega_c}\right)^2 \beta_h\hbar\omega_h\coth(\beta_c\hbar\omega_c/2) + \left(\frac{\alpha}{\omega_h}\right)^2 \beta_c\hbar\omega_c\coth(\beta_h\hbar\omega_h/2)\right)\,. \tag{3.33}$$

These are the hallmarks of *friction*. As we attempt to go faster, we produce heat (entropy production increases) and lower the efficiency and effectiveness of our efforts. But this "quantum friction" phenomena extends far beyond the quasistatic limit. To see this, we need to consider an arbitrary change in frequency.

3.3 More General Friction

We have seen that near-quasistatic operation leads to friction. But what about other ways of changing the frequency, far from the quasistatic regime? These too generally lead to friction. To see this, we need some generic way to consider the change of energy along the adiabat. It can be directly determined from the equations of motion that the following

quantity is conserved by the adiabatic dynamics:

$$X = \frac{\langle \hat{\mathrm{H}} \rangle^2 - \langle \hat{\mathrm{L}} \rangle^2 - \langle \hat{\mathrm{C}} \rangle^2}{\hbar \omega^2} \,. \tag{3.34}$$

This should not be too surprising, as this is the Casimir of the dynamical Lie algebra involved. A dynamical Lie algebra is one generated by commutation by the Hamiltonian, and therefore one that allows us to determine the dynamics. The Casimir of such an algebra would always be constant under the action of the Hamiltonian defining it.

To maximize cooling, we need to minimize the energy at the end of the adiabatic expansion stroke. The constancy of X implies that this energy would be obtained when $C = L = 0$, which characterizes a thermal state. Note that this is the same minimal value that is reached in the quasistatic limit. Generally, however, it would not be achieved. Even if we start from a thermal state, changing the frequency will lead to the build-up of correlations and a deviation from equipartition. The constancy of X therefore implies that generically the energy H_C at the end of the adiabat will be higher than the quasistatic minimum. As the energy gap $H_{Ceq} - H_C$ determines the cooling, this implies that a generic cycle will cool less than the quasistatic cycle. In other words - friction will lower the cooling per cycle.

What about entropy generation? The lowered Q_c means that less entropy is being decreased in the cold bath, increasing entropy production. The higher H_C also means that a higher H_D would be reached with the same τ_c. This in turn will tend to lead to a higher H_A, especially if the compression adiabat is also fast so friction is added there as well. And this will mean a higher Q_h, so a greater increase in the entropy generated in the hot bath. Overall, then, entropy generation should generally increase. Quantum friction will increase entropy generation.

From similar arguments we can see that the COP would also be lowered. We have already determined that cooling per cycle will be decreased. Since H_C will be higher, the work needed to do the expansion adiabat must also be higher. Since both H_D and H_A

increase it is not clear whether the work gained in the compression adiabat will generally increase or decrease, but if we assume that H_D is close to the equilibrium value H_{Heq} then it can only increase marginally so that any considerable amount of friction should take us to an H_A significantly above the quasistatic limit, causing us to need to invest more work W and thereby lowering the COP.

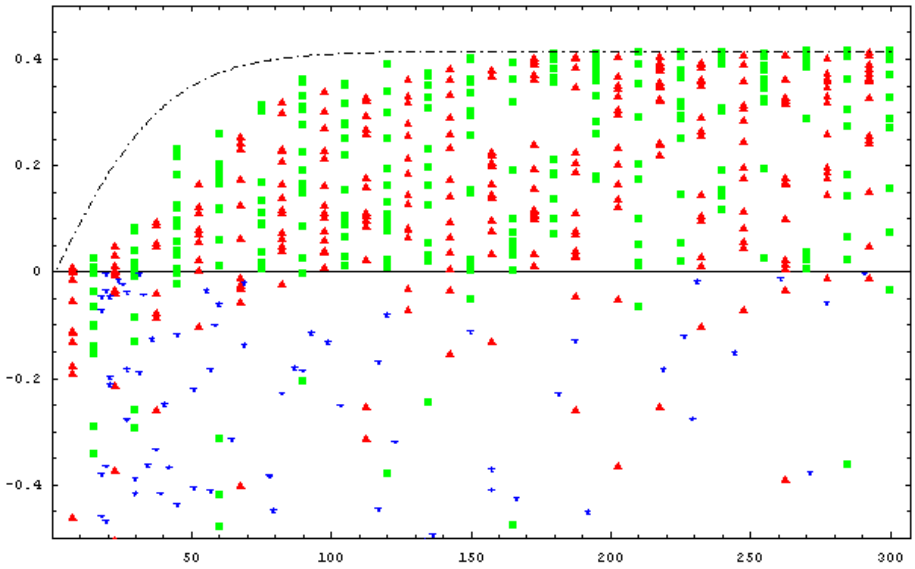
We can therefore expect that changing the frequency in finite time would result in quantum friction, leading to lowered performance and efficiency and an increase in heat exhaust. This is borne out analytically at the limit of instantaneous change [19, 20], where all three parameters are significantly below the quasistatic cycle; the equations are too complex to show here, but see figure 3.2 for an example. More generally, numerical simulations of the cycle with linear ($\omega(t) = \omega_0 + \alpha t$) or exponential ($\dot{\omega}/\omega = \text{const}$) changes in frequency show decreased performance as well (see figure 3.2).

We therefore see that in every respect - decreasing performance, generating heat, and decreasing efficiency - a fast change generically acts like friction, even far from the quasistatic limit.

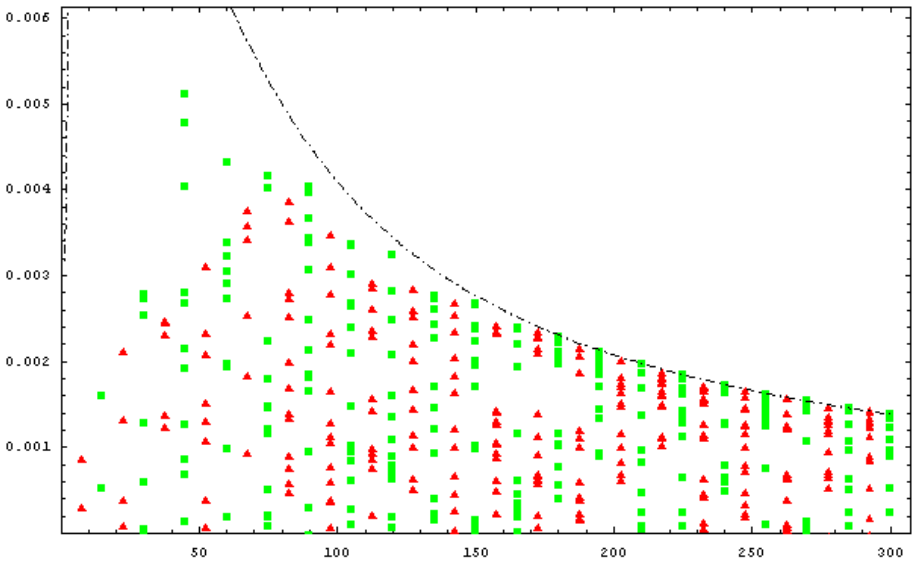
3.4 Quantum Friction in General

Quantum friction extends well beyond the model I have considered here. Consider a quantum system with a discrete energy spectrum (we will further assume non-degeneracy for simplicity). An ensemble will have some average energy $E = \sum p_i E_i$ (where $p_i = p(E_i)$ is the probability to find the system in a certain energy eigenstate). A rapid change in external constraints corresponds to a change in some external semi-classical field in the system's Hamiltonian. If the change to the external field is slow enough, the quantum adiabatic theorem assures us that there will be no changes in the energy populations and therefore the change in the energy will be due only to the change in energy levels. The energy in such a "quasistatic" process changes minimally in this sense.

Now consider a faster change. The rapid change in energy levels can now lead to



(a) Cooling Per Cycle



(b) Cooling Rate

Figure 3.2: The decrease in performance in finite time - a numerical example for specific parameters. The two plots are of the (a) cooling per cycle and (b) cooling rate for linear (red triangles) and exponential (green squares) frequency change along the adiabatic strokes. Note that the exponential form is superior, leading to higher Q_c and R. The frictionless limit is marked by a line. Blue stars (drawn for Q_c only) are cycles with an instantaneous adiabat; in this example, the resulting friction is so great that none manage to produce positive cooling - they fail to cool the cold bath.

population changes, changing the energy beyond the "minimal" quasistatic change of the energy levels themselves. For simplicity, let us first assume that we start from the ground state (zero temperature). Then we can only lose population density to higher states, so that we can only reach a higher (or equal) energy compared to the quasistatic change. Thus we receive a "resistance" to velocity: when we strive to derive the system quickly we need to invest more work.

This process, by itself, is reversible. Simply reversing the field-change protocol will yield back the original state and the original energy. The evolution is reversible because it is a unitary dynamics. However, consider appending a non-unitary step to the process. Now we leave the field at its final value for a time, while bringing the system into contact with a heat bath at its original temperature (zero, in this case). This will induce irreversible thermalization and loss of information about the original state. Such thermalization will convert the extra energy required into extra heat in the environment.

This line of reasoning can be generalized for a finite temperature. Consider the energy change during some external-field change. Allahverdyan and Nieuwenhuizen proved that, barring level-crossing, for a system initially at a thermal state the minimal energy is reached by a quasistatic process [33, 34]. Their derivation hinges on realizing that the state's eigenvalues do not change during unitary evolution, and that for a smooth enough field-change protocol the adiabatic theorem ensures absence of transitions between states. Their results hold beyond the thermal state, to any initial state with decreasing occupations in the energy eigenbasis. The condition of no level crossing allows us to estimate the time scale required for the quasistatic limit as related to the inverse of the minimum energy level gap [35–38]. We emphasize that if level-crossing does occur, Allahverdyna and Nieuwenhuizen show that the quasistatic protocol may not be the optimal one. A quasistatic timescale for the adiabatic theorem can still be defined in this case [39, 40]. Most importantly, the requirement for no level crossing is always satisfied for a single varying field parameter, a result known as the non-crossing rule [41, 42].

In this discussion we separated the thermalization phase from the driving phase. In

realistic cases, however, driven systems will be at least weakly coupled to thermal environments. The two processes will occur simultaneously, implying that any external driving will be converted through dissipation to some quantum friction.

In addition to thermaliztion, residual interactions with the environment may lead to dephasing noise. This will also be the effect of imperfect control over the external field. Since pure dephasing is identical to a weak measurement of the momentary energy, one would expect it to draw the state towards the momentary energy eigenbasis, thereby approximating the quasistatic process and thus acting as a "quantum lubricant" that reduces friction. This indeed happens in some cases [43]. However, in at least some cases pure dephasing of this sort can decrease efficiency [44]. The effect of dephasing noise in general is not sufficiently understood, but it does not appear to eliminate quantum internal friction entirely even when it does function as a lubricant.

Our specific model was an example of such a quantum internal friction process. We will see below that, formally, there are frequency-change protocols that avoid generating friction (in these solutions the state returns to its quasistatic analog at some finite time t_f.) Using such protocols, it is seemingly possible to drive the system at a finite rate and still avoid friction. However, although it appears that such processes can occur in arbitrarily short time [44–46], that requires an arbitrarily large available energy. This can be understood in light of the energy-time uncertainty relation: an infinitely fast process requires an infinite variance in energy. An instantenous frictionless solution is therefore not viable, and any finite-period solution will result in dissipative losses to the environment (when $t < t_f$). In at least some cases, frictionless solutions also seem unstable under dephasing noise [44]. In the realistic case of weak coupling, then, some frictional loss is unavoidable (although it may be negligible in practice).

While I have focused on the harmonic oscillator, separate analysis reveals similar results for spin systems [44, 47], and under continuous coupling to the bath for a three-level system [16]. Since the underlying features that give rise to the phenomena are the non-commutative nature of the Hamiltonian at different times and the irreversible nature

of thermalization, there is good reason to believe that this kind of quantum friction would be endemic in realistic systems.

3.5 A Frictionless Cycle

Returning to the harmonic oscillator, we argued above that changing the frequency along an adiabat will generally produce inferior results, as it will lead to the development of correlations and loss of equipartition (cf. section 3.3). But is there a way to carefully change the frequency so that we will end up with none, and thus conserve the full efficacy of the quasistatic cycle at finite time? It turns out that there is a simple way to do so.

Looking at the equations of motion along the adiabat (equation 3.5), it is natural to consider that case where the dimensionless measure of adiabicity $\mu \equiv \frac{\dot{\omega}}{\omega^2}$ is constant. In this case it is possible to solve the equations explicitly by changing the time variable to $\theta = \int_0^t \omega(t')dt$. Then factoring out the term $\mu\vec{1}$ and diagonalizing the time-independent part with the eigenvalues $\lambda_0 = 0$ and $\lambda_\pm = \pm\Omega$ where $\Omega = \sqrt{\mu^2 - 4}$ leads to the adiabatic propagator $\mathscr{U}_a$ for H, L, C along an adiabatic stroke,

$$\mathscr{U}_a(t) = \frac{\omega(t)}{\omega(0)}\Omega^{-2}\begin{pmatrix} \mu^2 c - 4 & \mu\Omega s & 2\mu(c-1) \\ \mu\Omega s & \Omega^2 c & 2\Omega s \\ -2\mu(c-1) & -2\Omega s & \mu^2 - 4c \end{pmatrix} \tag{3.35}$$

where $c = \cosh(\Omega\theta)$, $s = \sinh(\Omega\theta)$, and $\theta(t) = -\log(\frac{\omega(0)}{\omega(t)})/\mu$.

To understand this solution consider the extreme case where $\omega_h \to \infty$. Then at the end of the hot thermalization segment we have $E_B = \frac{1}{2}\hbar\omega_h$, and the energy at the end of the expansion adiabat becomes

$$E_C = \frac{1}{2}\hbar\omega_c \frac{1}{\Omega^2}\left(\mu^2 \cosh(\Omega\theta_c)\right) - 4 \tag{3.36}$$

$$\theta_c = -\frac{1}{\mu}\log(\frac{\omega_h}{\omega_c})\,. \tag{3.37}$$

For very fast expansion $\mu \to \infty$, $E_C = \frac{1}{4}\hbar\omega_c(\frac{\omega_h}{\omega_c} + \frac{\omega_c}{\omega_h})$. As $T_c \to 0$ and $\omega_c \to 0$ this means that $H_C = \frac{1}{4}\hbar\omega_h$ which becomes larger than H_{Ceq} so that the cooling stops because of the friction. Very fast operation thus leads to the arrest of all cooling. In contrast, very slow operation $\mu \to 0$ as expected leads to the quasistatic result as $H_C \to \frac{1}{2}\hbar\omega_c$. At this limit since $\tau_{expansion} \to \infty$, the cooling rate is zero $R \to 0$.

The surprising point is that it is possible to find an additional frictionless point at critical times. Because c and s are regular oscillatory trigonometric cosine and sine for $|\mu| < 2$, we will return to the same values as for $\theta = 0$ at critical times. At these points $c = 1$ and $s = 0$, which makes the matrix at equation (3.35) a unit $\hat{1}$ and returns us to the original values up to a factor $\omega(t)/\omega(0)$. This occurs for the first time at the critical point

$$\mu^* = -\frac{2\log(\omega_h/\omega_c)}{\sqrt{4\pi^2_{\mathrm{Log}}(\omega_h/\omega_c)^2}} \tag{3.38}$$

$$\tau_{expansion} = (1 - \frac{\omega_h}{\omega_c})/(\mu^*\omega_h)\ . \tag{3.39}$$

Asymptotically as $T_c \to 0$ and $\omega_c \to 0$, the critical terms approach $\mu^* \to -2$ and with it the time allocation $\tau_{expansion} = \frac{1}{2}\omega_c^{-1}$. Combining this with equation (3.30) we obtain that as we try to cool towards the zero temperature the cooling rate drops as

$$R \propto T_c^2\ . \tag{3.40}$$

This result is better than a linear frequency change, for which we received $\tau \propto \omega_c^{-2}$ and $R \propto T_c^3$. It establishes that frictionless solutions exist and can be effective, but are there other frictionless solutions? And more importantly, are there ones that take a shorter time? That would allow even lower exponentials.

3.6 The Optimal Frictionless Cycle

Any frictionless cycle maximizes the cooling per cycle Q_c. But maximizing the cooling rate requires finding the frictionless cycle that takes the least time to perform. It is possible to determine it using optimal control theory [22]. For the purposes of this presentation, however, it would be more intuitive to present a geometrical derivation [48].

3.6.1 The Q^2-P^2 Plane

The critical stroke in the Otto refrigeration cycle, that determines the cooling, is the adiabatic expansion (B to C). For ease of analysis I now wish to move from the familiar variables $\{\hat{\mathrm{H}},\hat{\mathrm{L}},\hat{\mathrm{C}}\}$ to the time-independent ones $\vec{V}=\{\hat{\mathrm{Q}}^2,\hat{\mathrm{P}}^2,\hat{\mathrm{Q}}\hat{\mathrm{P}}+\hat{\mathrm{P}}\hat{\mathrm{Q}}\}$. These variables are not directly affected by a change in frequency, so are invariant to an instantaneous jump in frequency. As the ideal solution will involve such jumps, turning to these variables eases its derivation. The equations of motion along an adiabatic stroke (cf. equation (3.5)) in these new variables are

$$\frac{dV_1}{dt}=\frac{1}{m}V_3 \tag{3.41}$$

$$\frac{dV_2}{dt}=-kv_3 \tag{3.42}$$

$$\frac{dV_3}{dt}=-2kV_1+2/mV_3\ , \tag{3.43}$$

and the constant of the motion X is

$$X=4V_1V_2-V_3^2\ . \tag{3.44}$$

Taking equations (3.41) and (3.42) together, we receive that the change in Q^2 and P^2 is related, so that for constant k their dynamics is always along a straight line in the $\{P^2,Q^2\}$

plane.

$$\frac{dV_2}{dV_1} = -km \tag{3.45}$$

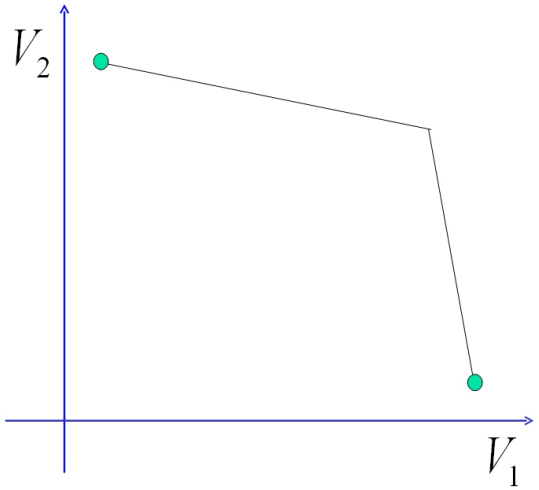


Figure 3.3: The initial and final points, and the optimal trajectory between them, schematically drawn on the $\{V_2, V_1\}$ plane. At thermal equilibrium, including the initial and final points, the state is on this plane, with $V_3 = 0$. The straight lines represent arbitrary maximal and minimal slopes, and therefore minimal and maximal spring constants (cf. equation (3.45)), that define the optimal trajectory.

Our geometric proof of minimal time will be made in this plane. We shall assume that we have some limitation on the maximal and minimal spring constants (frequencies) that we can operate the cycle with, k_{max} and k_{min}. We allow k_{min} to be negative. To determine the time required to conduct the change, we will assume for simplicity that we are starting from at thermal equilibrium $L = C = 0$ with the hot bath; this is not a limitation as we are seeking a bound, and starting from a state that is not yet fully thermalized would only be worse. In the old variables thermal equilibrium is characterizes by $\{H, L, C\} = \{E, 0, 0\}$; in the new variables, thermal equilibrium is characterized by $\{Q^2, P^2, XP + PX\} = \{E/k, mE, 0\}$ (where k is the spring constant and m the mass). A quasistatic adiabat would lead us to a

new equilibrium, at $\{E_i\sqrt{k_f/k_i}/k_f, E_i\sqrt{k_f/k_i}m, 0\}$. Both points are on the $\{P^2, Q^2\}$ plane, and (since $k_f < k_i$) the initial point is above and to the left of the final one (see figure 3.3).

3.6.2 The Optimization Problem

We are seeking to minimize the time it takes to go from the initial to the final point. The time along the adiabat in the new variables can be integrated from equation (3.41) with the aid of equation (3.45), and is

$$\tau = \int_{V_1(i)}^{V_1(f)} \frac{m}{\sqrt{4V_1V_2 - V_3^2}} dV_1 \ . \tag{3.46}$$

From this equation it is evident that to minimize the time for the transition we must, for each $V_1 = Q^2$, seek the largest V_2 possible. If forced to choose, it is furthermore better to adopt small values of V_2 at high (rather than low) values of V_1. Our task is hence reduced to seeking such a path from the initial to the final point, where the slope along the trajectory must be confined by $-km$, and $k_{min} < k < k_{max}$. Simple geometrical observation (cf. figure 3.3) suffices to see that such a trajectory would consist of two parts: starting at the initial point we will proceed with minimal k so as to keep V_2 as large as possible, and maintain it for as long as possible until we are forced to turn to k_max to dive back and reach the final point.

The switching point between the two extreme slopes can be found, again, from geometric considerations. The values of the switching point $\vec{V}_s$ are determined by the need to connect the initial and final points on the plane. We must demand, for example, that

$$V_2(f) = V_2(i) - mk_{min}(V_1(s) - V_1(i)) - mk_{max}(V_1(f) - V_1(s)) \ . \tag{3.47}$$

Physically, we are starting the expansion adiabat at the frequency ω_h and ending it at ω_c. The solution above implies that the shortest way to do so (while ending up at the quasistatic result) is a three-jump "bang-bang" solution, where the frequency is changed

instantaneously three times at the appropriate moments.

$$\omega(t) = \begin{cases} \omega_h & t = 0 \\ \omega_{min} & 0 < t < \tau_1 \\ \omega_{max} & \tau_1 < t < \tau_1 + \tau_2 \\ \omega_c & t = \tau_1 + \tau_2 \end{cases} \tag{3.48}$$

The times τ_1 and τ_2 can be found by considering the actual solution of the equations of motion (in the new variables) for constant k. Starting from $\vec{V}_i$, we can examine how long it takes to reach the switching point, and this will set the first time. We can determine the second time similarly. This analysis reveals the critical times to be [24]

$$\tau_1 = \frac{1}{2\sqrt{|k_{min}|/m}} \text{acosh}\left(\frac{2k_{min}(k_{max}+k_f)\sqrt{k_i} - (k_{min}+k_{max})(k_{min}+k_i)\sqrt{k_f}}{(k_{max}-k_{min})\sqrt{k_f}(k_{min}-k_i)}\right) \tag{3.49}$$

$$\tau_2 = \frac{1}{2\sqrt{k_{max}/m}} \text{acos}\left(\frac{2k_{max}(k_{min}+k_i)\sqrt{k_f} - (k_{min}+k_{max})(k_{max}+k_f)\sqrt{k_i}}{(k_{min}-k_{max})\sqrt{k_i}(k_{max}-k_f)}\right) . \tag{3.50}$$

What are reasonable limits on k_{min} and k_{max}? We have already established that large ω_h and small ω_c are advantageous. It therefore makes sense that we would set ω_h as large as we physically can, and ω_c as small as we can. Assuming that $k_{max} = m\omega_h^2$ and $k_{min} = m\omega_c^2$ leads to the relatively simple expression for the total adiabat's time: [21],

$$\tau = \frac{1}{2}\left(\frac{1}{\omega_c} + \frac{1}{\omega_h}\right) \text{acos}\left(\frac{\omega_h^2\omega_c^2}{(\omega_h+\omega_c)^2}\right) \to \frac{1}{\sqrt{\omega_h\omega_c}} , \tag{3.51}$$

where the limit is for low cold frequencies $\omega_c \to 0$. Note that we have here $\tau_{adi} \propto \omega_c^{-0.5}$, which by equation (3.30) implies

$$R \propto T_c^{1.5} . \tag{3.52}$$

It is possible, however, to consider $k_{min} < 0$. This implies that the piston binding the

gas particles becomes a repelling potential for a limited time before convulsing back into a potential well. A realistic scenario for such a possibility is the "adiabatic cooling" phase of cooling ions and atoms trapped in harmonic wells. In these cases an harmonic potential is established to trap atoms, and is slowly dropped to cool the atoms quasistatically. This, naturally, takes considerable time. Our method allows a shortcut to adiabicity, providing a way to conduct the same change in finite time. Under these circumstances, the trap's maximum strength is typically equal to its maximal possible (repelling) force, $k_{min} = -k_{max}$. Assuming further that $k_{max} = k_i$ one obtains

$$\tau_1 = \frac{\operatorname{acosh}\left(\frac{k_f+k_i}{2\sqrt{k_f k_i}}\right)}{2\sqrt{\frac{k_i}{m}}} \to -\frac{\log\left(\frac{kf}{ki}\right)}{4\sqrt{ki/m}} \tag{3.53}$$

$$\tau_2 = \frac{\pi}{4\sqrt{ki/m}} \tag{3.54}$$

so that the total time at small frequencies (i.e. $k_f \to 0$) scales as $\tau \propto \log(\omega_c^2)$.

More generally, if we assume that k_{min} and k_{max} are limited experimentally independently of ω_c, one obtains

$$\tau_1 \to\propto \frac{(k_{min}-k_i)(k_{min}-k_{max})}{2k_{min}^{3/2}}\sqrt{-\frac{mk_{min}^2}{(k_i-k_{min})^2(k_{max}-k_{min})^2}}\log(\omega_c) \tag{3.55}$$

$$\tau_2 \to\propto \frac{(k_{max}-k_{min})(k_i+k_{min})m}{2k_{max}k_{min}}\omega_c + \frac{\pi+\operatorname{acos}\left(\frac{-k_{max}-k_{min}}{k_{max}-k_{min}}\right)}{2\sqrt{\frac{k_{max}}{m}}};. \tag{3.56}$$

This implies that $\tau \propto -\log(\omega_c)$ is the best scaling achievable. In analogy to the argument in section 3.1.4, we can proceed to ask how the cooling rate $R = G/\tau_{adi}$ will be affected. Assuming that the expansion stroke dominates or at least sets the scale, we can ignore the other strokes' time. Within the expansion stroke, τ_1 dominates. We can therefore consider

$R = G/\tau_1$. Taking the derivative with respect to ω_c leads to the the extremum condition

$$\frac{2(-1+\log(\omega_c))\sinh(\frac{\mathscr{R}_c}{2})\sinh(\frac{\mathscr{R}_c-\mathscr{R}_h}{2})}{\log(\omega_c)} + \mathscr{R}_c\sinh(\frac{\mathscr{R}_h}{2}) = 0\,. \tag{3.57}$$

Now as $\omega_c \to 0$ its log goes to $-\infty$, which makes the "-1" negligible. Tentatively removing it we are left with a condition that is dependent only on $\mathscr{R}_c$ and $\mathscr{R}_h$ so that the optimal ω_c should be kept to keep $\mathscr{R}_c$ constant, i.e. $\omega_c^* \propto T_c$. This does, however, leave us with a reminder

$$-\frac{2\sinh(\frac{\mathscr{R}_c}{2})\sinh(\frac{\mathscr{R}_c-\mathscr{R}_h}{2}}{\log(\omega_c)}\,. \tag{3.58}$$

As $\log(\omega_c) \to -\infty$ this expression approaches zero, so that at the limit we are indeed correct to set $\omega_c^* \propto T_c$. Considering the expression for R, this implies that it scales as

$$R \propto -T_c^1/\log(T_c)\,. \tag{3.59}$$

This is far better than the previous results, of a scaling of $R \propto T_c^3$ for the linear case, or the $R \propto T_c^{1.5}$ for the previous frictionless solution. In all cases, however, the cooling rate drops faster than the limitation of the second law requires, $R \propto T_c^1$.

3.7 General Notes

We have investigated several ways to operate the Otto cycle. In all cases we were able to reach the limit set by the second law of thermodynamics on the cooling per cycle, $Q \propto T_c^1$. In all cases the cooling rate was further limited by the cycle time, which exploded to infinity at the limit of zero temperature. This is a dynamic manifestation of the third law: it is impossible to cool at the absolute zero, as a cooling cycle would require infinite time. The cooling rate thus dropped to zero faster than $R \propto T_c^1$. We believe that these results are general, and hold regardless of the specific model: it is possible to reach the cooling limit

$Q_c \propto T_C$, but the cooling rate must drop faster as we approach zero temperature. We have achieved such a low drop, $R \propto -T_c/\log(T_c)$, that we have effectively established that the Otto cycle is an ideal cycle in the sense that no other cycle can hope to be meaningfully faster at low temperatures.

In all cases we have found that to maximize the cooling rate we need to follow the cold temperature to zero, $\omega_c^* \propto T_c$. When ω_c cannot be lowered beyond a certain value, we receive an exponential drop in cooling as $Q_c \propto (n_{Ceq} - n_{Heq})$ is reduced, until at some critical temperature $T_c^{(crit)}$ the equilibrium population n_{Ceq} becomes too large and the cooling stops altogether. We will see below that this result extends beyond our particular model, and we suggest that it, too, is universal. The system's relevant energy gap must in some way be "in resonance" with the temperature $k_B T_c$, and drop linearly with it, for the exchange of heat to be efficient. This result is consistent with the quant of heat transfer in quantum wires, $\frac{\pi^2 k_B^2 T_c}{3\hbar}$ [49].

The optimal way to schedule the operation turned out to be a "bang-bang" solution, where the external controls are changed instantly. This too we believe to be surprisingly generic. Work by Seifert *et al* [50] has shown that optimizing minimal work in other and general models typically requires sudden shifts and discontinuities in the control fields. While the solutions do not generally correspond to the bang-bang solution, these results do indicate that in general one should expect discontinuous protocols to be best.

When our results were published [21, 22] they garnered significant interest from the atomic cooling community. Our analysis was initially limited to positive frequencies, and it was immediately apparent that atomic cooling allows also imaginary frequencies, or in other words repelling harmonic potentials, and that this would allow faster cooling rates. This allowed us to develop our more general results above.

Our results indicate that a transition between two thermal states can only be done in some minimal finite time. This result is related to the quantum speed limit for transition between two orthonormal states [51], but this is the first time a bound on the transition speed between thermal states has been established. This aspect of our work was challenged

when it was argued that the transition can be accomplished arbitrarily fast by certain choices of $\omega(t)$ [52]. In all such cases, however, the choices ignored our bounds on k. Under some restrictions, at least, it was shown [53] that the bound on the time is related to the time-energy uncertainty principle. Shorter times require larger energy resources to make the transition, so that restricting the available energy (or, equivalently, the oscillator's frequency) restricts the time needed to perform the transition. We therefore expect a universal ban on instantaneous transitions, as long as energy-resources are kept in mind.

Finally, the specific requirement for three jumps in our solution was called into question, as it was noted that more jumps are advantageous if k_{max} is large enough [54]. We note that such cycles always involve "retrograde" motion, from the initial point to points with *lower* V_1. But this point corresponds to an equilibrium at $k > k_i$, so that it is simpler (and, for the refrigeration cycle, better) to establish an initial equilibrium at this higher k. When $k_{max} = k_i$ no such trajectories are possible [24].

Chapter 4

Spin systems

We consider a different quantum system wit the purpose of generalizing our results. We have so far only considered the emergence of the third law of thermodynamics in an harmonic-oscillator system. I now turn to consider spin systems. I review previous results, and show that they imply that the absolute zero is not, ultimately, achievable.

4.1 Spin Otto Refrigerator

A spin system analogous to the harmonic oscillator studied in Chapter 3 was studied by Feldmann and Kosloff in a series of papers [43, 44, 47, 55–57]. They consider two interacting spins under the influence of a time-dependent external field,

$$\hat{\mathrm{H}} = \frac{1}{2}\hbar J(\hat{\sigma}_x^1 \otimes \hat{\sigma}_x^w - \hat{\sigma}_y^1 \otimes \hat{\sigma}_y^2) + \frac{1}{2}\hbar\omega(t)(\hat{\sigma}_z \otimes \hat{1}^2 + \hat{1}^1 \otimes \hat{\sigma}_z^2) \equiv \hbar J\hat{\mathrm{B}}_2 + \hbar\omega(t)\hat{\mathrm{B}}_1 \ , \quad (4.1)$$

which they operate in an Otto cycle. A key difference from the harmonic-oscillator case is that the energy gaps in the system are proportional to $\Omega = \sqrt{\omega^2 + J^2}$ instead of simply to ω. It is therefore impossible to lower the energy gaps to zero as the temperature is lowered. Remember that for the harmonic oscillator we have observed that (to maximize the cooling rate) the energy gap should drop linearly with the temperature $\Delta E = \hbar\omega \propto T_c$

(cf. equation 3.29). This result has also been found in a three-level system [58]. Since this cannot be maintained for the two-spin Otto refrigerator, this system cannot reach the ultimate limit allowed by the third law - a cooling rate faster than $R \propto T_c$. Instead, the optimal cycle is characterized by a adiabatic strokes with duration $\tau_{adi}^{(min)} = \frac{1}{J}(\frac{\omega_c}{\Omega_c} - \omega_h\Omega_h)\sqrt{\left(\frac{2\pi}{\text{asin}(\frac{\omega_c}{\Omega_c})-\text{asin}(\frac{\omega_h}{\Omega_h})}\right)^2 - 1}$ [44], which at the limit of cold temperatures approaches a constant $\tau_{adi} \propto 1/J$ (and therefore does not explode). The optimal cooling rate therefore is proportional to an exponent $R \propto exp(-\hbar J/k_B T_c)$ [57], as expected from our general analysis (cf. section 2.3.1).

Assuming finite resources, the finite energy gap even leads to a sharp cut-off temperature below which no cooling is possible. In Chapter 3, we deduced that for the harmonic oscillator optimal (frictionless) solutions implied $\beta_c\omega_c < \beta_h\omega_h$. For the two-spin system, the analogous result is $T_c \geq \Omega_c T_h/\Omega_h$. Since $\Omega_c \geq J$, this implies the minimum temperature $T_c \geq JT_h/\Omega_h$. Cooling to zero temperature is therefore impossible given finite resources (a finite field-strength ω_h). The above exponential is only obtained under the assumptions of infinite resources.

For the two-spin cycle, a sharp cut-off exists even given the unphysical assumption $\omega_h \to \infty$. At this limit the population after equilibration with the hot bath will all be in the ground state, at energy $H_B = -\hbar\Omega_h$. After a quasistatic adiabat it will be at the corresponding ground state $H_C = -\hbar\Omega_c$. If some quantum friction exists, the energy would be higher by some small amount $H_C = -\hbar\Omega_c(1-\delta)$. For the cycle to cool, this must be lower than the equilibrium energy, $-\hbar\Omega_c(1-\delta) < H_{eq}^{(C)} = -\hbar\Omega_c(1-exp(-\hbar\Omega_c/k_B T_c))$, where the last inequality is at the cold temperatures limit $k_B T_c \ll \hbar\Omega_c$. At the limit of $T_c \to 0$, this implies that any deviation from the quasistatic result will lead to a finite temperature $T_c(\delta)$ below which no cooling is possible. The possibility of cooling to the absolute zero therefore requires not only the unphysical assumption $\omega_h \to \infty$, but also the existence of frictionless cycles. Even a slight deviation from the frictionless conditions, due to some uncontrollable noise or friction, will lead to a finite minimal temperature [44].

I note that this is not the case for the harmonic oscillator. The corresponding condition for the harmonic oscillator Otto cycle is $\hbar\omega_c(\frac{1}{exp(-\beta_c\hbar\omega_c)-1}+\frac{1}{2}+\delta) < \hbar\omega_c(\frac{1}{exp(-\beta_h\hbar\omega_h)-1}+\frac{1}{2})$. Since ω_c can go to zero as T_c does, it is now possible to go to zero temperature while maintaining this condition, so that a finite deviation from the quasistatic solution is allowed for the harmonic oscillator. Our result that the zero temperature is reachable for the harmonic oscillator should be robust to small noise.

These results seem to imply that finite energy gaps, under finite resources, lead to a minimal temperature beyond which cooling is not possible. To explore this further, we now turn to examine cooling through another spin system: algorithmic cooling.

4.2 Algorithmic Cooling

A key type of restriction we have so far not considered is using only finite (N-level) systems. We have seen above that limiting the energy resources leads to limitations on cooling, and limiting the amount of energy levels is a related and, therefore, promising limit that we wish to explore in this section.

We will thus consider cooling a *finite* quantum target system $\mathscr{T}$, using a *finite* quantum system $\mathscr{S}$ as a refrigerator. We will further assume that we have access to an effectively-infinite hot heat bath, $\mathscr{B}$, however. The above analysis makes it clear that the finitude of resources matters, so we will restrict ourselves to a refrigerator $\mathscr{S}$ with some finite number of energy levels, N. We will furthermore, for simplicity, assume that near the absolute zero the target system can be considered as a two-level system. We are thus left with two resources at our disposal: (a) we can manipulate the refrigerator and target systems, inducing unitary transformations (by e.g. changing an external field), or (b) we can couple part of the refrigerator to the (infinite) hot heat bath. Our goal is to cool the target system as much as possible using these resources. This is a generic recipe for cooling, so that I consider establishing a minimal temperature in this context to be equivalent to establishing it generally.

A similar bound was established by investigations into algorithmic cooling. Algorithmic cooling (AC) was first suggested by Boykin *et al* [59] as a method to initialize the register of a quantum computer. Let us consider a register, or chain, of n two-level systems. Each is considered to initially be at some *bias* ε, defining the one-TLS state

$$\rho_\varepsilon = \frac{1}{e^\varepsilon + e^{-\varepsilon}} \begin{pmatrix} e^\varepsilon & 0 \\ 0 & e^{-\varepsilon} \end{pmatrix}, \tag{4.2}$$

where the bias is related to the temperature through the relation $\varepsilon = \Delta E/2k_BT$, where ΔE is the relevant energy gap and T the temperature. A bias of zero corresponds to infinite temperature, while a bias of infinity to zero temperature[1]. The goal is to cool $m < n$ spins on this chain, initializing them into (approximately) their ground state, usually denoted $|0\rangle$. The ability to initialize a quantum register in this manner is vital to quantum computation.

In AC, this is accomplished through two kinds of steps:

- **Compression** The state of the n-bit register is manipulated through some (specific, state-independent) unitary transformation. The target m bits are cooled in the process, and the rest of the chain is necessarily heated up as a result. This can be seen from the fact that a unitary transformation does not change the total entropy of the chain, so that when part of it is cooled (lowered in entropy) the rest must heat up (increase in entropy).

- **Thermalization** Part of the heated-up part, the "refrigerator", is coupled to an environment, and undergoes complete thermalization. This step allows one to "reset" the heated-up qbits to lower (environment) temperatures.

[1] Bias is sometimes (e.g. [59]) defined according to the linearization

$$\rho_\varepsilon = \begin{pmatrix} (1+\varepsilon)/2 & 0 \\ 0 & (1-\varepsilon)/2 \end{pmatrix}$$

so that zero temperature corresponds to a bias of 1. Our definitions are more useful for our purposes. Note that the two definitions coincide for small bias, which is the focus of algorithmic cooling.

The two steps are repeated cyclically, an arbitrary number of times. At each compression step the compression is bound by a (Shannon-derived) bound. The thermalization stage brings in more resources, allowing the algorithm to cool beyond this limit.

Boykin's original algorithm was refined and advanced in many of papers (e.g. [60–63]). It was given a thermodynamical analysis by Rempp [61, 64]. For our purposes, however, it is better to consider the work of Schulman *et al* [65, 66], that considered arbitrary unitary operations between thermalization steps. Schulman *et al* were able to prove that there is a bound on how low AC can push the bias of the m bits, and in particular showed that there is a bound to the bias of even a single qbit. We will use their results to argue, more generally, that no cooling, given finite resources, is possible beyond a certain minimal temperature. We must therefore consider their proof in some detail.

In algorithmic cooling one assumes, for simplicity, an initial state where all n qbits have the same initial bias. Schulman *et al* assume specifically an initial state of zero bias, or infinite temperature. This is simply the unit matrix, $\hat{1}$. What is important to the rest of the proof, however, is mainly that this state is diagonal.

We would be interested in cooling spin number 1, and shall assume that only spin n is thermalized in the thermalization step. Let us denote the initial density matrix as ρ_0. Then AC consists of applying a thermalization stroke i to obtain $i\rho_0$, followed by some arbitrary unitary operation u_1 to obtain $\rho_1 = u_1 i\rho_0$, and so on. Schulman *et al* demonstrate that when starting from a diagonal density matrix ρ_0, applying a permutation (which keeps the state ρ_1 diagonal) is always superior to other transformations, in the sense that it majorizes them. When a density matrix ρ_1 majorizes matrix ρ_0 (denoted as $\rho_1 \succeq \rho_0$), then (amongst other properties) the bias of the first spin is greater in ρ_1. In other words, the target system $\mathscr{T}$ that we want to cool is closer to zero temperature. To maximize cooling, we can therefore consider only permutations instead of general unitary operations.

To consider the effect of the thermalization steps, consider some initial $2^n x 2^n$ density

matrix

$$\rho_0 = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^{\dagger} & \rho_{22} \end{pmatrix} , \tag{4.3}$$

where the states $|0\rangle$ and $|1\rangle$ of the nth quit, the only one that gets to thermalize to ρ_ε, determine this division into blocks. Then the application of a thermalization stroke will result in

$$\rho_2 = \rho_\varepsilon \otimes (\rho_{11} + \rho_{22}) = \frac{1}{e^{\varepsilon} + e^{-\varepsilon}} \begin{pmatrix} e^{\varepsilon}(\rho_{11} + \rho_{22}) & 0 \\ 0 & e^{-\varepsilon}(\rho_{11} + \rho_{22}) \end{pmatrix} . \tag{4.4}$$

This implies that the probabilities along the diagonal density are changed in pairs, according to the transformation

$$p'_{\omega 0} = (p_{\omega 0} + p_{\omega 1}) \frac{e^{\varepsilon}}{e^{\varepsilon} + e^{-\varepsilon}} \tag{4.5}$$

$$p'_{\omega 1} = (p_{\omega 0} + p_{\omega 1}) \frac{e^{-\varepsilon}}{e^{\varepsilon} + e^{-\varepsilon}} . \tag{4.6}$$

The general problem is hence reduced to finding the right permutations to do in between thermalization steps, so as to maximize the bias of the first spin. After each thermalization stroke, we can jumble the probabilities, choosing which pairs to be acted on by the next thermalization stroke.

Note that on a logarithmic scale $z = \log(2^n p)$, the above transformation always pushes two values to be 2ε apart. The key to establishing the bound is to note that neighboring-probabilities stay at least as close to each other as that. Schulman *et al* arrange the probabilities in descending order $p_0 \geq p_1 ...$, and define as "partners" for each even corresponding state j the nearest probability $j+1$. Then for any two partners p and p' they

prove the critical relation

$$\|\log p - \log p'\| \leq 2\varepsilon \ . \tag{4.7}$$

This is correct for two reasons. First, Schulman *et al* begin at the initial "infinite temperature" density matrix $\rho_0 = \hat{1}$. This condition is then trivially satisfied. Secondly, Schulman *et al* demonstrate that for a state already satisfying the above assumptions applying a permutation plus a thermalization step will not increase the logarithmic distance between the two probabilities to more than 2ε.

Another key feature of the transformation is that it does not increase the mean of the probabilities on the logarithmic scale, z. At small bias the rescaled probabilities are set at 2ε around the mean, and this is the limit Schulman *et al* are concerned with. I note further that at very large bias the mean is decreased.

Together, these two features suffice to prove the bound on the bias. In the initial state, all 2^n probabilities are identical at 2^{-n}. Schulman *et al* define the new quantity $z = \log 2^n p$ so that all points are initially at zero. The application of a thermalization stage then moves each two points, chosen to be paired by the prior permutation, apart. It does so in a particular way, however, keeping them 2ε apart and not increasing their mean. The result is that no two points are ever driven more than 2ε apart, and that the mean of the overall distribution of points is never increased. No point can therefore move more than $2^n\varepsilon$ from the origin[2], or equivalently to a probability of less than $p_{max} = 2^{-n}e^{\varepsilon 2^n}$.

Notice, however, that in no place was it truly necessary to assume that we are dealing with a collection of two-level systems. It is enough to consider that we are dealing with some $N = 2^n$ level system. We need only designate the first spin as pertaining to the two-level target system $\mathscr{T}$ that we are trying to cool, and the last spin to a TLS effectively thermalized by the environment as part of our refrigerator. Without loss of generality, then, one can simply consider this a treatment of such an N-level system.

[2]Schulman *et al* actually also produce a complicated argument for a bound of $2^{n-1}\varepsilon$, but since the scaling is identical it is not of concern to us

Similarly, there was little actual need to assume the initial infinite temperature state, with uniform probabilities. All one really needed was a diagonal state. We can hence assume a more reasonable initial state, consisting of a thermal state for both the target spin and, separately, the rest of the N-level system. Since there is a finite number of probabilities, there would then be some finite ε such that for all pairs the proximity condition $\|\log p - \log p'\| \leq 2\varepsilon$ is satisfied. Assuming that the thermalization stroke will induce at least this bias, we can then proceed with the proof as given above. The only point one needs to be careful of is that the mean and initial points are no longer at zero, so that the situation is not symmetric and one must take that into account. Instead, the mean of z must be calculated and it is approximately proportional to $\frac{1}{N}\sum_i -\beta\Delta E_i \propto -\beta\Delta E$ where ΔE is a typical energy gap. I shall assume the relevant temperature is on the scale of the hot bath's temperature. The new bound for the distance in z is thus $-\beta_h\Delta E - N\varepsilon$, and since for the initial thermal state $\varepsilon \sim -\beta\Delta E$ this is $-\beta_h\Delta E(N+1)$. For high bias $z \propto \varepsilon$ so that the maximum bias in the macroscopic and cold-temperature limit is on the order of N.

In conclusion, we suggest that the quantum third law of thermodynamics is that no finite (N-level) system can be used to cool a target system to below a minimum temperature on the scale of

$$k_B T_{min} > \Delta E_c \frac{k_B T_h}{2\Delta E}\frac{1}{N}\,. \tag{4.8}$$

This result is speculative since we have not truly dealt with an N-level system starting from a general, coherent, state. One can also inquire into the effect of allowing more "spins", or larger subsystems, to thermalize in the thermal stroke. We do not expect this to meaningfully change the results, however, as the cooling "cycle" can be expanded to include spin-exchange operations instead of adding more thermalizing qbits. The consideration of larger target systems, and in particular degeneracy of the ground or first excited states, is also a cause for concern. And finally, our result is based on estimations of the relevant quantities (such as ΔE) and scaling, that may not be easy to determine or verify

for a specific system. Despite these caveats, I believe the above at least strongly suggests that the maximal bias achieved by any cooling method that uses an N-level quantum system as a refrigerator will increase polynomially with N, reaching infinite bias (zero temperature) only in the macroscopic limit $N \to \infty$.

Chapter 5

Conclusions

The laws of thermodynamics are emergent phenomena, arising from the microscopic underlying mechanics. While classical thermodynamics implies simply the impossibility of reaching absolute zero in finite time, quantum mechanics adds layers of complications that result in a more nuanced and meaningful third law of quantum thermodynamics. While a rigorous or general proof of this third law is still out of reach, the above investigations have revealed something of its contour. I suggest the following formulations, at various degrees of restriction on the available resources:

- It is impossible to cool, using finite resources, any finite quantum system below a certain minimal temperature T_{min}.
- Given an N-level refrigerator, the maximum obtainable bias scales as N, so that the minimal temperature is on the scale of the first energy gap of the cooled system and approaches zero in the macroscopic limit.
- Given finite energy resources, the minimal time required to cool the system to any given temperature drops with the energy so that infinite energy resources allow reaching the temperature in zero time.
- For any refrigeration process, but given finite energy resources, the maximum

cooling rate as one approaches the absolute zero drops asymptotically faster than the temperature does (faster than $R \propto T_c$).

- Near the absolute zero, given finite energy resources, the time required to draw an amount of energy from the finite system that is proportional to T_c goes to infinity as the system's temperature is reduced. This time can be reduced by investing more energy, but given finite energy resources it is always finite and scales in the above way.

- For refrigeration cycles operating in a fixed cycle time, the cooling rate will drop exponentially past a certain critical temperature.

- Cooling to the absolute zero requires an energy gap that scales with the temperature. If a minimal energy gap exists, through which the cooling is mediated, then refrigeration will stop sharply at some minimal temperature polynomial in this minimal energy gap.

In the course of my study, I have also showed that quantum friction reduces the effectiveness of refrigeration so that generically quasistatic processes are superior. Finite-time frictionless solution exist, however. While these are unstable in some systems (e.g. the two-spin Otto refrigerator) and disappear under even negligible noise from the environment, they are expected to be stable for other systems (e.g. the harmonic oscillator). I note, in this context, that the frictionless limit has since been effectively reached experimentally [67].

I have also shown that some minimal time is required in order to transition between two thermal states. This time is dependent on the energy resources available, in accordance with the time-energy uncertainty principle, so that infinite energy resources could diminish it to zero. Given finite resources, however, we have seen that it is impossible to drive the harmonic oscillator to a final thermal state in arbitrarily short times.

I have also shown that it is impossible to drive an harmonic oscillator to below the temperature achieved by a quasistatic process. This has great significance for attempts to cool atoms to ultra-low temperatures in harmonic traps and has already resulted in experiments attempting to implement the procedures that reach this limit [67–69]. While my results are technically limited to the harmonic oscillator, I believe they have far wider applicability. The attempt to establish similar bounds and optimal procedures for cooling atoms in non-harmonic traps is a current ongoing project [67], that I hope will bear fruit in the near future. These ideas are also currently being employed to the study of frictionless quantum transport [70, 71].

Appendix A

List of Publications

My PhD research was published in four papers, three of which with me as the principal author.

- Y. Rezek and R. Kosloff. Irreversible performance of a quantum harmonic heat engine. *New Journal of Physics*, 8:83, 2006.

  This paper [19] summarizes the results of my master's thesis [18], but includes also more insights into the performance and thermodynamics of the Otto cycle. The relevant content is reviewed in the beginning of Chapter 3, and in sections 3.1.1, 3.1.2, parts of section 3.1.3, and the expression for the entropy in section 3.1.4.

- Y. Rezek, P. Salamon, K.H. Hoffmann, and R. Kosloff. The quantum refrigerator: The quest for absolute zero. *EPL (Europhysics Letters)*, 85:30008, 2009.

  In this paper [21] we describe the frictionless cooling solutions, including the first one we were able to obtain (section 3.5) as well as the optimal bang-bang solution (section 3.6 with $k > 0$). Our work relies on the following ("Maximum work in minimum time") article for the solution of the optimization problem.

- P. Salamon, K.H. Hoffmann, Y. Rezek, and R. Kosloff. Maximum work in minimum time from a conservative quantum system. *Physical Chemistry Chemical Physics*, 11(7):10271032, 2009.

  This work [22] discusses the optimization problem leading to the bang-bang solution. It relies on the previous paper ("The quantum refrigerator: the quest for absolute zero") for the thermodynamic significance. Note that Peter Salamon is the principal author.

- Y. Rezek. Reflections on friction in quantum mechanics. *Entropy*, 12(8):18851901, 2010.

  This review [23] discusses quantum friction in general. It includes results for the harmonic oscillator (section 3.3) and the more general treatment (section 3.4).

One more paper is at this time in the final stages of peer review, and should be published shortly.

- K.H. Hoffmann, P. Salamon, Y. Rezek, and R. Kosloff. Time-optimal controls for frictionless cooling in harmonic traps. To be published.

  In this paper [24] we extend the bang-bang solution to imaginary frequencies ($k > 0$). Some of its results are included in section 3.6. While the principal author is Karl Heinz Hoffman, the relevant results presented in this thesis were obtained by me.

In addition, I published one proceedings report.

- Y. Rezek and R. Kosloff. Quantum refrigerator in the quest for the absolute zero temperature. In *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, volume 6907, page 10, 2008.

  This is a report [20] on the progress in analyzing cooling by the harmonic oscillator up to this point. Its results are included in sections 3.1.4 and 3.2.

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במהלך מחקר זה, אנו גם הראנו בפעם הראשונה שקיים זמן מינימלי למעבר בין שני מצבים תרמיים. זמן זה קצר יותר ככול שיותר משאבי אנרגיה זמינים, ומתפוצץ כאשר הטמפרטורה הסופית שואפת לאפס המוחלט.

בדיוננו במערכות ספינים, אנו סוקרים תוצאות שהושגו עבור מעגל אוטו המשתמש בשני ספינים, וטוענים כי העובדה שקיים פער אנרגיה מינימלי מונעת את הקירור לאפס המוחלט.

אנו מנתחים את הקירור בצורה יותר כללית בהתבסס על "קירור אלגוריתמי". אנו סוקרים תוצאות קודמות שמראות שבעזרת אלגוריתם זה ניתן לקבוע את ההסתברות שרגיסטר של ספינים יהיה במצב היסוד רק עד גבול מקסימלי מסוים. אנו מכלילים את התוצאות הללו, וטוענים שמכך נובע שבכל מערך קירור סביר לא ניתן לקרר מערכת קוונטית סופית מעבר לטמפרטורה מינמלית (גדולה מאפס) מסוימת. טמפרטורה זו שואפת לאפס בגבול המקרוסקופי.

התוצאות שלנו מעידות שבתחום הקוונטי חוקי התרמודינאמיקה שונים במובן עדין. החוק השלישי או עקרון חוסר–ההשגה עדיין תקף, אך ניתן לשפרו על קביעת גבולות להתנהגות האסימפטוטית של קצבים וטמפרטורה מינימלית הגדולה מאפס. גבולות אלו לוקחים בחשבון עוד משאבים מעבר ל"מספר פעולות סופי", כולל פערי אנרגיה סופיים, משאבי אנרגיה זמינים, והגודל הסופי של המקרר והאמבטים.

תקציר

חוקי התרמודינאמיקה נחשבים ככלל כעולים מתוך חוקי המכניקה המיקרוסקופית. חלה התקדמות ניכרת בביסוס היווצרותם תחת תנאים קלאסיים. אולם, ההבנה של התרמודינאמיקה בהקשרים קוונטיים במובהק עודנה חסרה. התהוות החוק השלישי של התרמודינאמיקה הינה בעייתית במיוחד. בתזה זו, אנו מכוונים לשפר את הבנת התרמודינאמיקה הקוונטית על ידי שקילת ההיווצרות הדינמית של חוקי התרמודינאמיקה במערכות ומודלים מסוימים. אנו מתמקדים בפרט בניתוח קצב הקירור של מקרר הפועל על ידי חומר פעיל המורכב ממתנדים הרמוניים קוונטיים, ובניתוח הקירור במערכות ספינים.

לאחר סקירה קצרה של התרמודינאמיקה הקוונטית, אנו טוענים כי בהקשר קוונטי הניסוח הקלאסי של החוק השלישי הידוע כ"עקרון הבלתי–השגה" (אשר אומר שלא ניתן לקרר לאפס המוחלט במספר סופי של פעולות פיזיקליות) מוביל להשלכות מסוימות באשר לקצב הקירור. אלו חורגות מעבר לגבולות המושמים על הקירור בשל החוק השני של התרמודינאמיקה.

אנו פונים לדון ולנתח בפירוט מקרר קוונטי מסוים, שמהווה מקבילה קוונטית למעגל אוטו הקלאסי. במקום להשתמש בחלקיקים קלאסיים בבוכנה, החומר הפעיל מורכב מחלקיקים קוונטיים תחת פוטנציאל הרמוני (דוחה או מושך). מגע עם אמבט חום ממודל בעזרת דינמיקה לינדבלדיאנית (חיובית שלמה), בהתאם לתורת המערכות הקוונטיות הפתוחות. אנו מדגימים שבמגל הגבול החומר הפעיל נמצא תמיד במצב קוהרנטי כללי, ומוצאים את הביטויים עבור אנטר ופיית וון–ניומן ושנון שלו. אנו מזהים שמורה חדשה של התנועה, הקשורה לקזימיר של אלגברת לי הרלוונטית.

ניתוח תרמו דינמי של המקרר מראה כי בגבול הקוואזי–סטטי (שינוי איטי במידה אינסופית של הבקרות החיצוניות) מעגל הגבול משיג את ההתנהגות האסימפטוטית הטובה ביותר שבאפשר עבור הקירור לכל מעגל, בהתאם להגבלב המוטלת על ידי החוק השני. אני מפתחים ביטויים מפורשים ליעילות, הקירור בכל מעגל, וייצור האנטרופיה. אנו מראים שקצב הקירור בשיאו כשר פער האנרגיה של המתנד פרופורציונלי לסקלת האנרגיה של טמפרטורת האמבט הקר. אזי קצב הקירור מוגבל בהתאם לדיוננו הכללי.

אנו מוצאים גם שניסיון לזוז מהר יותר, מעבר לגבול הקוזי–סטטי, מביא באופן כללי לחיכוך קוונטי שפוגע בקירור. אנו דנים בחיכוך הקוונטי במערכת זו ובכלל, וטוענים כי באופן כללי הוא יוביל להפסדים לחיכוך בכל שיטת קירור.

יחד עם זאת, אנו מראים כי קיים מעגלים "חסרי חיכוך" שיכולים להשיג את הקירור לכל מעגל של הגבול הקוואזי–סטטי בזמן סופי. אנו מוצאים דוגמה פשוטה ישירות, ובטיעון מסובך יותר מוצאים את הפתרון המהיר ביותר. כאשר אנו מרשים פוטנציאל הרמוני הודף, אנו מראים שהפתרון המיטבי מגיע לקצב קירור היורד עם הטמפרטורה אסימפטוטית בצורה הקרובה לגבול המותר על ידי עקרון הבלתי–השגה והחוק השני.

עבודה זו נעשתה בהדרכתו של
פרופ' רוני קוזלוב

מכונות חום
ומערכות קוונטיות:
לקראת החוק השלישי

חיבור לשם קבלת תואר דוקטור לפילוסופיה

מאת

יאיר רזק

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