

Imperial College London
Centre for Doctoral Training in Controlled Quantum Dynamics
Department of Physics

The resource theory of quantum thermodynamics

Matteo Lostaglio

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Supervised by Dr. David Jennings & Prof. Terry Rudolph

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*I could be bounded in a nutshell and count myself a king of infinite space,
were it not that I have bad dreams.*

Hamlet

*Thermodynamics is the study of the restrictions on the possible properties of matter that follow
from the symmetry properties of the fundamental laws of physics.*

*H. B. Callen,
Thermodynamics and an introduction to thermostatistics, II edition*

Declaration of originality

I hereby declare that the following thesis is composed of my own original work, developed during my PhD at Imperial College in the Controlled Quantum Dynamics group. All published and unpublished work of others has been appropriately referenced and acknowledged.

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List of publications

This thesis is based upon the following publications and pre-prints

1. **M. Lostaglio**, D. Jennings, T. Rudolph, *Thermodynamic resource theories, non-commutativity and maximum entropy principles*, [arXiv:1511.04420](#) (2015) – Ref. [1].
2. K. Korzekwa, **M. Lostaglio**, J. Oppenheim, D. Jennings, *The extraction of work from quantum coherence*, [New J. Phys. 18 023045](#) (2016) – Ref. [2].
3. **M. Lostaglio**, M. P. Mueller, M. Pastena, *Stochastic independence as a resource in small-scale thermodynamics*, [Phys. Rev. Lett. 115, 150402](#), Editors' suggestion (2015) – Ref. [3].
4. **M. Lostaglio**, K. Korzekwa, D. Jennings, T. Rudolph, *Quantum coherence, time-translation symmetry and thermodynamics*, [Phys. Rev. X 5, 021001](#) (2015) – Ref. [4].
5. **M. Lostaglio**, D. Jennings, T. Rudolph, *Description of quantum coherence in thermodynamics requires constraints beyond free energy relations*, [Nat. Comm. 6, 6383](#) (2015) – Ref. [5].

Other works not included in the thesis are

1. K. Korzekwa, **M. Lostaglio**, *Classical noise and the structure of minimal uncertainty states*, [Phys. Rev. A 93 062347](#) (2016).
2. K. Korzekwa, **M. Lostaglio**, D. Jennings, T. Rudolph, *Quantum and classical entropic uncertainty relations*, [Phys. Rev. A 89, 042122](#) (2014) – Ref. [72].

An updated list of publications can be found on ArXiv at the following [link](#).

Abstract

Planck found, when attempting to describe the way in which hot bodies glow, that energy at microscopic scales often comes in discrete chunks. Thus began the long and intimate relationship between the field of thermodynamics, which explores our ability to manipulate heat and other energy transfers between macroscopic systems, and quantum mechanics, which explains the dynamics of individual microscopic systems. Even as both our technology and our theoretical investigations have extended to ever-smaller devices, our understanding of quantum effects on thermodynamics has remained almost exclusively limited to the quantized nature of energy. There is much more, however, to quantum theory than energy quantization. In this thesis we focus on the property of quantum coherence, the ability of quantum systems to emulate Schrödingers cat and somehow be neither dead nor alive, but something completely different altogether.

We provide a simple and elegant formulation for the processing of coherence in thermodynamics, relying on the fact that thermodynamical processes possess an underlying time-translation symmetry. This fact allows us to quantify the ways in which coherence can play an active role, facilitating otherwise impossible thermodynamic transformations. We argue that coherence should be thought of as a distinctly quantum-mechanical thermodynamic resource. By considering an isolated quantum system connected, for some period of time, to a thermal bath, we give fundamental limitations on how coherence can be irreversibly manipulated. These limitations are related to those dictated on energy transfer by the second law of thermodynamics. Others topics that are investigated here is what is the role of correlations at the smallest scales and the conversion of quantum coherence into work.

It has long been appreciated that thermodynamics is subtly interlinked with the notion of information. This work provides evidence that, to apply the laws of thermodynamics to the smallest systems around us, we must develop deeper insights into the nature of quantum information.

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1 Introduction and summary of results

1.1 What is this? Should I care?

If, as it happens, you find yourself at a party of famous new theories, you may meet a very old guy with a new-age look and ask him “Hey, what’s up? I sort of know you from undergrad but can’t quite recognise you” and he may give you the (slightly embarrassed) answer “Oh, no, I’m just here with my granddaughter”. It would not take you long to discover that his granddaughter is the world-famous theory of entanglement (many before suspected some degree of kinship [7, 8]) and he is Mr Thermodynamics himself, the man who supposedly can make you cry every single time you contradict him [9]; what is really odd, however, is that now his granddaughter is on stage introducing the puzzled audience to her ideas about how grandpa should look like in the age of quantum information theory. The result is what she enthusiastically calls a “resource theory of thermodynamics”. The reaction is mixed. I overheard three main sorts: 1. She is deceiving an entire generation of physicists; 2. This is the greatest talk I have ever heard in my life, and I am including Terry Rudolph’s youtube video “Quantum theory: it’s unreal”; 3. This is cool and useless as Marvin Minsky’s useless machine.¹

So, what is the resource theory of quantum thermodynamics? It is an attempt to talk precisely about the resources involved in a task, once some general thermodynamic limitations are set in place. In the theory of entanglement the limitation is that two or more parties do not share a quantum channel. In thermodynamics, it is about the thermality of the environment and the fact that energy is microscopically conserved.

As one may expect, such theory inherits the qualities and the weaknesses of the theory of entanglement. Due to its bottom-up approach, it is best suited for the thermodynamics of a small number of quantum systems. Somehow similarly, we understand entanglement better in the bipartite scenario and many-body mixed state entanglement is an untamed creature.

From a more condensed-matter perspective this may look a bit puzzling, as thermodynamics is naturally associated with ideas such as macroscopicity and thermodynamic limit. The claim, however, is that regimes not previously considered under the jurisdiction of thermodynamics actually are within its domain. When we are dealing with a lot of physical systems, a sufficient description of what happens to them can be obtained by keeping track of the most likely events only; due to the law of large numbers, what happens in any given instance will – with overwhelming probability – coincide with what

¹The machine has a single switch. The switch activates a lever that switches the machine off. *Cool.*

typically happens. A description then emerges in which expectation values become increasingly important and a small number of measurable parameters are the only quantities characterising the thermodynamics of a system. At the other end of the spectrum, far from the thermodynamic limit, fluctuations dominate due to the small number of events and systems involved; in this mostly uncharted territory standard statistical mechanics techniques lose their ability to predict what is going to happen. New developments disrupted this picture in two ways: on one hand, we can now experimentally control single quantum systems with unprecedented precision; on the other hand, new tools from the field of one-shot information theory increasingly allow us to crack these problems from the theoretical side.

So, why do some get frustrated at the resource theory approach? In my experience, typically it is because they find it unhelpful to understand the physics of specific implementations they care about. They are usually right, but this is sometimes beyond the point. It is a little bit like being upset by the theory of entanglement because, say, it assumes that it is perfectly fine for Alice to create a gigantic cluster state, as long as she does not share it with Bob. At least as unrealistic is the assumption, in the resource theory of thermodynamics, that one can prepare arbitrary thermal states at a fixed temperature. And we could go on with the disparaging comparisons: does the theory of entanglement tell us anything about how to create and sustain entanglement in the first place? Does the resource theory of thermodynamics tell us anything about the propagation of heat along a 1D spin chain? Why does the theory of entanglement not include as a free operation the creation of quantum correlations among two nearby qubits, even if this can be realised with near perfect fidelity in an ion trap? Why does the theory of thermodynamics not include general unitaries on a qubit as free operations, even if these can be easily realised by shining a laser on it? The theory of entanglement only marginally captures the issues on our way to a quantum ENIAC and, arguably, the resource theory we describe in this thesis will be at best only marginally relevant to the technical problem of building nano-engines.

So, perhaps, if we want to understand what is the point of the resource theory of thermodynamics, we should ask why people did not throw entanglement theory out of the window (perhaps we should)? The answer must have something to do with the fact that the theory offers tools to precisely quantify and assess a phenomenon previously only qualitatively understood; to develop a general framework to think about how useful entanglement is and in what different “flavours” it comes; to see how in some situations one can define useful golden standards and why there is a kind of “bound” entanglement that resists being converted into this form. I hope the resource theory of thermodynamics will be taken by experts in the field on quantum thermodynamics in this complementary (rather than adversarial) way: as a useful tools to get precise intuitions regarding inequivalent ways in which a quantum state can be out of equilibrium, and why some ways may be more useful than others; about what abstract resources allow some transformations, and what is fundamentally quantum about all of this. Quantum thermodynamics experts

can help quantum information ask the right questions; conversely, the resource theory can help understand some general structural properties beyond what is valid under a specific model.

The resource theory of thermodynamics is a rather novel subject, and barely existed when I began my PhD. Many questions are still unanswered and only time will show if it proves a fruitful way of thinking about thermodynamic phenomena. Personally, I live under the illusion that I've not wasted my PhD, as I've learned a lot from it. Being generically sceptical of all-encompassing frameworks, I have never expected this approach to be a general-purpose formalism for quantum thermodynamics; if you are looking for this, you are bound to feel disappointed one way or another. But if you are still bearing with me, I will now outline what is the content of this thesis. Before doing that, however, I will try to clarify what is *not* included here.

1.2 *Noutline* - an outline of what is *not* in this thesis

Thermodynamics is traditionally a theory of macroscopic system in equilibrium. The large number of microscopic degrees of freedom are irrelevant for the measurement of macroscopic observables over timescales extremely long compared to the typical atomic dynamics; a small number of thermodynamic variables thus emerges as a complete description at such a coarse scale. In this context, a unique function – called entropy – is assumed to fully capture the properties of equilibrium states through an extremum principle [10].

In this thesis, on the other hand, we will focus mostly on what is sometimes called fine-grained thermodynamics, where a small number of quantum systems interact with a dissipative environment. Instead of focusing on the properties at equilibrium only, we will be interested in the possible evolutions of the atomic degrees of freedom from a non-equilibrium state to another. Common to standard approaches is the centrality of the principle of energy conservation (first law of thermodynamics). On the other hand, the postulate that a single entropy function captures the thermodynamic accessibility of one state from another is not tenable.

Since the regime we are interested in is far from the thermodynamic limit, a traditional statistical mechanics approach cannot be applied. As systems display quantum properties such as coherence and entanglement, in this thesis we will discuss to what extent conventional thermodynamic principles capture these quantum-mechanical aspects. Of course, some quantum properties also feature in macroscopic equilibrium systems. These are usually studied from a quantum statistical mechanics perspective and include the effect of particle statistics and the study of phase transitions [11]. These important subjects are not, however, the object of this thesis.

Another approach we can compare with is fluctuation theorems (FTs). Loosely speaking, these important relations link the fluctuating work performed on a microscopic system we drive out of equilibrium to the free energy at equilibrium [12]. This is a situation

closer to the regime considered in this thesis; however, despite quantum formulations of FTs exist, they are usually based on projective energy measurements that destroy the most important quantum features we want to study. Hence, the resource theory approach has the opportunity to give insights beyond those gathered in the context of FTs. In this thesis, we will not discuss FTs.

What distinguishes the framework developed in this thesis from the previous results is that the resource theory approach satisfies three basic requirements:

- It deals with non-equilibrium systems;
- It deals with non-macroscopic systems;
- It is suited to the study of intrinsically quantum-mechanical effects such as coherence and entanglement.

The study of this “extreme quantum regime” is a foundational question about thermodynamics, but the miniaturisation of technology and the behaviour of biological systems lead to conjecture that a deeper understanding of non-equilibrium in a setting that satisfies the above requirements would be beneficial.

Now that we said what is *not* in this thesis, we outline the content of the various chapters.

1.3 Outline

- Chapter 2 [review]: this thesis is about some aspects of the resource theory of thermodynamics that I have been working on throughout my PhD. As such, it should not be regarded as a complete review of the topic. This first chapter is a relatively self-contained discussion of the preliminaries needed to understand the rest of the work. It is divided into two main parts: a first section dealing with the notion of partial ordering among vectors, with relevant results on the theory of majorisation and its extensions, as well as an initial discussion justifying why we need these notions in thermodynamics in the first place; and a second part introducing the concept of resource theories and briefly presenting two crucial examples, i.e. thermodynamics and asymmetry. In the rest of the thesis I will give for granted some concepts widely used in quantum information theory, such as quantum channels and their equivalent characterisations (essentially the first few chapters of J. Watrous lecture notes²).
- Chapter 3: the exploration of small-scale thermodynamics begins with a discussion of the role of correlations. In the thermodynamic limit, general arguments say that correlations require work to be set up. On the other hand, we will see that in single-shot thermodynamics the *lack* of correlations can be an extremely useful resource. In

²These can be found at <https://cs.uwaterloo.ca/~watrous/LectureNotes.html>

fact, every transition that is allowed macroscopically becomes possible microscopically as well, if we can access a source of stochastic independence. Among other things, this allows in principle reliable work extraction from microscopic systems, overcoming the problem of fluctuations without allowing any failure probability in the protocol. This chapter is based on the published work [3].

- Chapter 4: here we begin our investigation of the role of quantum coherence in thermodynamics, the main topic of this thesis. We will see that the resource theory of thermodynamics is characterised by an underlying symmetry principle that constrains our ability to manipulate quantum coherence in the presence of a heat bath. More strongly, we can show that any consideration uniquely based on notions such as free energy cannot capture the full set of restrictions present at the quantum scale. We give new constraints, akin to second laws for quantum coherence, based on a generalisation of the free energy quantifying how much a state breaks time-translation symmetry. We discuss some of the consequences such as work-locking (in which the work used to generate a state remains trapped in its coherence) and the emergence of classicality in the thermodynamic limit. This is based on the published work [5].
- Chapter 5: we now take full advantage of the symmetry principles described in Chapter 4, showing that even the generalised laws of coherence dissipation are still missing important symmetry structures. This is understood by decomposing quantum states in “coherence modes”, representing superpositions of increasing energy difference. For each of them, we give general constraints on the amount of coherence that is unavoidably dissipated in the presence of a heat bath, for some given heat exchanges with the bath. These limitations are related to those imposed on the transfer of energy by the second law of thermodynamics. We present applications such as coherence transfer and coherence merging, comparing the constraints coming from symmetry only and those that entail further thermodynamic irreversibility as well. This chapter is mainly based on [4], even though some refinements are due to forthcoming work with K.Korzekwa and A.Milne.
- Chapter 6: in this chapter we thoroughly analyse the issue of work extraction from general states carrying quantum coherence. Previous investigations found accordance to traditional approaches, setting the limit of average work extraction from a single quantum system to be equal to the (quantum) free energy change in the state. We find, however, that these works make, one way or another, classicality assumptions on the machine used to achieve the extraction, or degrade in various ways ancillae that remain unaccounted for. We present protocols where all systems are treated quantum-mechanically and show that there exists a well-defined classical limit recovering the above-mentioned free energy result. This essentially corresponds to having at our disposal a machine with a classical field carrying infi-

nite coherence - but our framework has the advantage of making precise statements about the degradation of such field. On the other hand, we find that, for finite coherence resources, not all the work can be extracted. Nevertheless – exploiting a recent intuition of J.Åberg – we show that we can use coherence to our advantage without ever degrading the coherence resources of the machine. These quantum protocols, however, fail short of the classical efficiency. This is based on the published work [2].

- Chapter 7: this part contains preliminary results regarding questions that stemmed naturally from the previous considerations. The common theme is to overcome some of the limitations of the resource theory formalism and connect to other approaches. It is divided into three sections. In the first one, we introduce the paradigm of Elementary Thermal Operations. This is done by first defining a physically motivated set of stochastic processes, showing that these are associated with a simple thermodynamic toy model and finally suggesting a quantum generalisation (this is partially based on [13]). The second part deals with the question of evolution in time of quantum coherence and the role of Markovianity in the theory - connecting to a language more familiar to open quantum systems experts (this contains results from a forthcoming work with K.Korzekwa and A.Milne). Finally, the third section suggests a new route to finding genuine quantum effects in thermodynamics, discussing the role of non-commutativity in the theory. The focus is on how commonly used considerations (such as the maximum entropy principle and complete passivity arguments) all agree in the commuting case but lead to different answers in the non-commuting scenario. This is based on parts of the pre-print [1].

2 Preliminary results

2.1 Ordering non-equilibrium

2.1.1 Standard thermodynamics is about ordering, not dynamics

Despite its name, standard thermodynamics is not about *dynamics*. It is, rather, mostly concerned with the notion of ordering among equilibrium states.

Consider a textbook thermodynamic question such as the following. We have a square box of volume V , containing an ideal gas at pressure P and temperature T . One face of the box can be turned into a movable piston (perhaps removing a locking mechanism). The piston can be attached to a weight of known mass in a gravitational potential, initially at a height L . So, the initial state can be described as $X = (T, P, V, L)$ (see Fig. 2.1). The weight may be used to do work on the gas by compressing it, or we may aim to raise the weight by allowing the gas to expand. Once things have settled down, the system will be described by new variables $X' = (T', P', V', L')$. The central question in thermodynamics is to know what transitions are possible, i.e. what states are accessible from X :

$$X \xrightarrow{?} X'. \quad (2.1)$$

If X' is accessible from X , we will write $X \succ X'$.

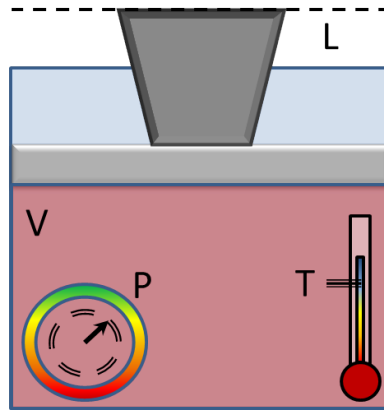


Figure 2.1. A standard thermodynamic setup. A gas in a box of volume V , at temperature T and pressure P , a weight of known mass at height L and a piston that can be transformed into a movable element. The equilibrium state of the gas is characterised by $X = (T, P, V, L)$.

The relation $\succ$ of thermodynamic accessibility from one state to another is easily seen to have at least the properties of a *partial ordering*, once we group into equivalence classes

[X] all states X that can be reversibly converted into each another.¹ In fact, the relation among distinct classes is reflexive, antisymmetric and transitive.²

The thermodynamic entropy S is a tool to determine such ordering. In textbook thermodynamics an implicit assumption is often made:

$$X \succ X' \Leftrightarrow S(X) \leq S(X'). \quad (2.2)$$

What this takes for granted, often without discussion, is that there exists a *total ordering* among all equilibrium states. A partial ordering $\succ$ is called total when any two states are *comparable*. In other words, given any two states X and X' in distinct thermodynamic classes, it is either $X \succ X'$ or $X' \succ X$. This is typically the case for transformations between equilibrium states (see Fig. 2.2) and is sometimes called Comparison Hypothesis [14, 15].

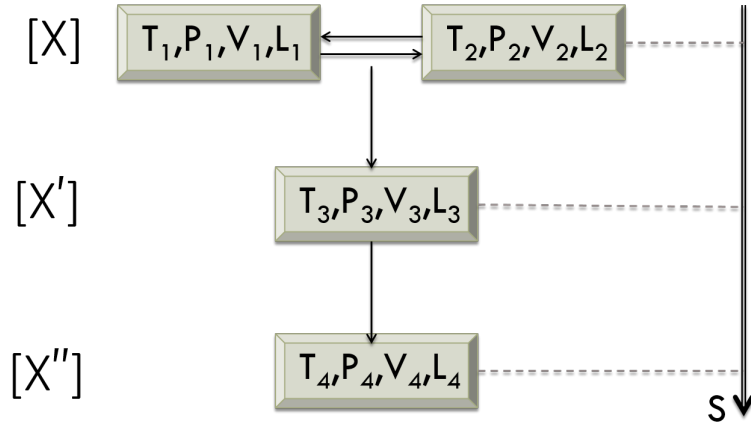


Figure 2.2. Equilibrium and total ordering. Equilibrium thermodynamics has the structure of a total ordering. This coincides with the possibility of completely capturing the thermodynamics of the system by means of a single entropy functional S . In this example, given $X_i = (T_i, P_i, V_i, L_i)$, $X_i \rightarrow X_j \Leftrightarrow S(X_i) \leq S(X_j)$.

Characterising accessibility relations in non-equilibrium thermodynamics is much more complicated. The crucial property that is lost is exactly the total order among states. This may be expected given that the state space is wildly more complex [16]. Consider for example what happens in the above example when we compress the gas quickly.³ If we do not wait for things to settle, the state of the gas will be an out of equilibrium state A , characterised by some unspecified parameters that will depend on the physics of the system. By repeating the experiment a second time, starting from the same equilibrium state X and either following the same or another protocol, we may generate a different non-equilibrium state B .

¹[X] = { Y | $Y \succ X$ and $X \succ Y$ }.

²A relation $\succ$ is reflexive if $X \succ X$, antisymmetric if $X \succ X', X' \succ X \Rightarrow X' = X$ and transitive if $X \succ X', X' \succ X'' \Rightarrow X \succ X''$.

³An important disclaimer: this should *not* be understood as an accurate thermodynamic model of such situations. It is just an introductory *toy* example whose aim is to present some of the issues at hand.

Assume we can introduce an appropriate extension of the state space, capturing the relevant parameters of the non-equilibrium physics we wish to describe. This is a non-trivial task, and may be not possible to carry it out in general. However, we want to discuss here what are the general features of non-equilibrium thermodynamics, assuming that such a theory can be constructed. In particular, operationally we are interested in knowing what non-equilibrium states can be obtained from an initial equilibrium state $X = (T_1, P_1, V_1, L_1)$.

It is a reasonable expectation that, in general, the operations at our disposal do not allow us to transform neither A into B nor B into A , even if leaving them to equilibrate they may settle down to the same equilibrium state $Y = (T_2, P_2, V_2, L_2)$ (see Fig. 2.3(a)). Hence, in this case, the relation of thermodynamic accessibility is *not* a total ordering, as A and B are incomparable.

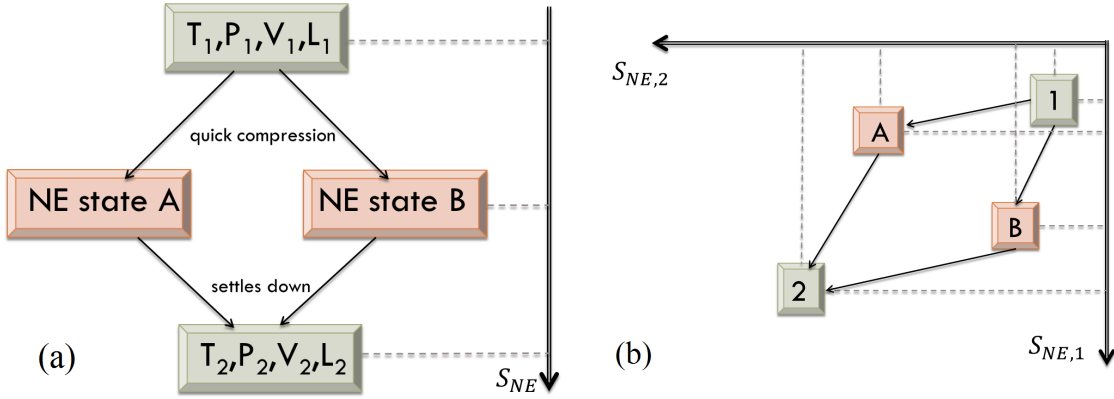


Figure 2.3. Beyond total ordering. (a): the thermodynamic ordering of the non-equilibrium example considered is not a total ordering. No single non-equilibrium entropy functional can characterise it. For example, S_{NE} in the picture fails to distinguish between the possibilities $A \rightarrow B$, $B \rightarrow A$, $A \leftrightarrow B$, or none of these. (b): introducing two non-equilibrium entropies $S_{NE,1}$ and $S_{NE,2}$ solves the problem in this toy model. Note that we used a shortened notation to indicate the various states.

Let us try to extend the entropy functional to non-equilibrium states and denote such extension S_{NE} . Entropy is like a shadow of the thermodynamic ordering on the real line. You can convince yourself that, in this non-equilibrium toy example, no choice of S_{NE} can completely characterise the ordering of states (in the sense of Eq. (2.2)). In fact, Eq. (2.2) would require S_{NE} to be an isomorphism from the set of relevant thermodynamic states (in our toy example $\{X, A, B, Y\}$, a partially ordered set including some non-equilibrium states) to the real line (which is a totally ordered set). Such mapping does not exist.

On the other hand, if we introduce *two* non-equilibrium entropy functionals, then the ordering of this example can be fully characterised, as shown in Fig 2.3(b). In other words,

$$X \succ Y \Leftrightarrow S_{NE,1}(X) \leq S_{NE,1}(Y), \quad S_{NE,2}(X) \leq S_{NE,2}(Y). \quad (2.3)$$

Of course, any realistic example will involve many (in general, infinite) out-of-equilibrium states with a complicated structure among them.

Hopefully this discussion has hinted at what concepts need to be introduced and formalised:

1. We need a precise notion of thermodynamic process “ $\longrightarrow$ ”. This will be discussed later, when we review the concept of *Resource Theories*.
2. We then need to characterise the ordering induced on the set of non-equilibrium states by the chosen notion of thermodynamic processes. In particular, we will need refined versions of the standard constraint “entropy increases”.

The second point naturally leads to the branch of mathematics that studies important notions of partial ordering. In the next section we give an introduction to this topic, trying to also give hints suggesting where the connection to thermodynamics arises.

2.1.2 Ordering states: from entropy to majorisation

In the previous discussion we suggested that many problems in thermodynamics can be reformulated as a question of ordering between thermodynamic states. The systems under consideration in this work are typically small quantum systems whose energy spectrum is quantised, and given by a set of energy levels $\{E_k\}$. In thermodynamics a special role is played by the equilibrium Gibbs distribution,

$$\mathbf{g} = \frac{e^{-\beta E_k}}{Z}, \quad Z = \sum_i e^{-\beta E_i} \quad (2.4)$$

where $\beta = 1/(kT_B)$ is the inverse temperature and Z is called partition function. This describes the equilibrium state of a system in contact with a large heat bath. However, we will be interested in generalising this to non-equilibrium states, whose population over different energy levels does not follow a Gibbsian distribution $\mathbf{g}$, but is described by a generic probability vector $\mathbf{x}$. Hence, we will be interested in studying how thermodynamic transformations define a partial ordering between these probability vectors.

In thermodynamics, we are used to defining “state functions”, such as entropy. In other words, we assign to every state of a system scalar quantities that, intuitively speaking, should measure the amount of “disorder” or, in Jaynes’ terms, the lack of knowledge within a given description of a system [17, 18]. We will now need a stronger version of this concept. This is captured by the notion of majorisation. Given a vector $\mathbf{x} \in \mathbb{R}^n$, denote by $\mathbf{x}^\downarrow$ the vector $\mathbf{x}$ sorted in non-increasing order. Then

Definition 2.1. $\mathbf{x}$ majorises $\mathbf{y}$, denoted $\mathbf{x} \succ \mathbf{y}$, if and only if

$$\sum_{i=1}^k x_i^\downarrow \geq \sum_{i=1}^k y_i^\downarrow, \quad k = 1, \dots, n-1, \quad \sum_{i=1}^n x_i = \sum_{i=1}^n y_i. \quad (2.5)$$

Example 2.2. Let $\eta = (1/3, 1/3, 1/3)$ and $e = (1, 0, 0)$. Then for all $x \in \mathbb{R}^3$ probability distributions, we have $e \succ x \succ \eta$. However, $\succ$ is not a total ordering among vectors. Take $y = (2/3, 1/6, 1/6)$, $z = (1/2, 1/2, 0)$. Then, neither $y \succ z$ nor $z \succ y$.

An alternative, more geometrical, definition can also be given, which is easily seen to be equivalent to the previous one:

Definition 2.3. Let $L(x)$ be the piecewise linear curve in $\mathbb{R}^2$ obtained by joining the origin and the points $(k, \sum_{i=1}^k x_i^\downarrow)$, for $k = 1, \dots, n$. We say that $L(x) \succ L(y)$ if and only if the curve $L(x)$ lies all above $L(y)$ and the two curves end at the same height.

The last requirement becomes trivial if x and y are both probability distributions. The curve $L(x)$ is called *Lorenz curve* and it is not difficult to check that $L(x) \succ L(y)$ if and only if $x \succ y$ (see Fig. 2.4).

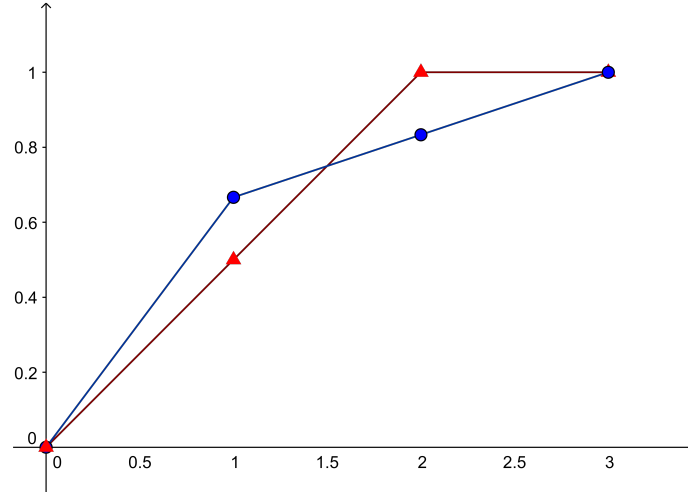


Figure 2.4. Majorisation curves. Given any probability distribution x , we can define a majorisation curve as in Def. 2.3. A distribution x majorises y if and only if the Lorenz curve of x is all above that of y . Neither of the two distributions x and y majorises the other, as their corresponding Lorenz curves intersect.

An operational interpretation to majorisation is given by the following theorem ([19], Chapter 2):

Theorem 2.4 (Hardy, Littlewood, Polya). $x \succ y$ if and only if there exists a stochastic matrix M satisfying

$$Mx = y, \quad M\eta = \eta, \quad (2.6)$$

where $\eta = (1/n, \dots, 1/n)$.

Stochastic matrices M satisfying $M\eta = \eta$ are also called doubly-stochastic or bistochastic. For completeness, a proof is given later in Aside 2.2. The fact that the uniform distribution η is a fixed point can be intuitively understood noticing that this is the state of maximum Shannon entropy, so that a process such that $M\eta \neq \eta$ would decrease entropy. However, it is fruitful to make the connection between majorisation and the

concept of entropy more precise. To do so, we define a natural class of functions – those that preserve the structure of majorisation:

Definition 2.5. A function $f : \mathbb{R}^n \rightarrow \mathbb{R}$ is called Schur-convex (respectively, Schur-concave) if and only if

$$\mathbf{x} \succ \mathbf{y} \Rightarrow f(\mathbf{x}) \geq f(\mathbf{y}) \quad (\text{respectively, } f(\mathbf{x}) \leq f(\mathbf{y})). \quad (2.7)$$

f is a homomorphism from the partially ordered set $(\mathbb{R}^n, \succ)$ to the ordered set of real numbers. In fact, we can think of each f as a possible entropy functional, as any physical process with the uniform distribution as a fixed point will not decrease it. Unsurprisingly, each f can only capture some aspects of the ordering.

The reason why majorisation is a more refined concept than entropy may be understood through an example. Consider the Shannon entropy, $H(\mathbf{x}) = -\sum_{i=1}^n x_i \log x_i$. Since $-x \log x$ is concave, $H(\mathbf{x})$ is Schur-concave (see Aside 2.1). So, $H(\mathbf{x}) \leq H(\mathbf{y})$ is a necessary condition for $\mathbf{x} \succ \mathbf{y}$. However, it is *not* sufficient, as the following example shows:

Example 2.6. Consider $\mathbf{y}$ and $\mathbf{z}$ from Example 2.2. From Theorem 2.4, no stochastic process with the uniform distribution as a fixed point can map $\mathbf{z}$ into $\mathbf{y}$, even though $H(\mathbf{z}) < H(\mathbf{y})$.

When coupled to Theorem 2.4, this tells us something important. The matrix M in Eq. (2.6) describes the transition probabilities of a stochastic process that has the uniform distribution as a fixed point and transforms $\mathbf{x}$ into $\mathbf{y}$. Due to Birkhoff's theorem ([19], Chapter 2), M can be decomposed as a convex mixture of permutations. So, intuitively, $\mathbf{x} \succ \mathbf{y}$ captures the idea that $\mathbf{y}$ is more mixed than $\mathbf{x}$. However, more strongly, $\mathbf{x} \succ \mathbf{y}$ also captures the existence of a stochastic process transforming $\mathbf{x}$ into $\mathbf{y}$. The decrease of $H(\mathbf{x})$ alone does *not* guarantee the existence of such physical process.

Remark 2.7. In terms of capturing the partial order induced by majorisation, two Schur-concave (or convex) functions that are linked by an affine transformations ought to be regarded as equivalent. In fact, if $\tilde{f} = af + b$, $a, b \in \mathbb{R}$, $a \neq 0$, then either $f(\mathbf{x}) \geq f(\mathbf{y}) \Leftrightarrow \tilde{f}(\mathbf{x}) \geq \tilde{f}(\mathbf{y})$ for all $\mathbf{x}$ and $\mathbf{y}$, or $f(\mathbf{x}) \geq f(\mathbf{y}) \Leftrightarrow \tilde{f}(\mathbf{x}) \leq \tilde{f}(\mathbf{y})$ for all $\mathbf{x}$ and $\mathbf{y}$. This may remind the reader the fact that thermodynamic entropy is also defined modulo an affine transformation.⁴

Mathematical Aside 2.1. Schur-concave functions toolbox [6]

Schur-concave functions on $(\mathbb{R}^n, \succ)$ can be constructed from concave functions on $\mathbb{R}$:
Let $h : \mathbb{R} \rightarrow \mathbb{R}$ be concave (convex). Then the function f

$$f(\mathbf{x}) = \sum_{i=1}^n h(x_i), \quad (2.8)$$

⁴We tend to take $a > 0$, as we conventionally define entropy as a functional increasing under thermodynamic processes.

is Schur-concave (Schur-convex).

Proof. We prove the statement for h concave (the other case is the same). From Theorem 2.4, $\mathbf{x} \succ \mathbf{y}$ if and only if $y_i = \sum_j M_{i|j} x_j$. Then, using $\sum_j M_{i|j} = 1$ and $\sum_i M_{i|j} = 1$,

$$f(\mathbf{y}) = \sum_{i=1}^n h \left(\sum_{j=1}^n M_{i|j} x_j \right) \geq \sum_{i=1}^n \sum_{j=1}^n M_{i|j} h(x_j) = \sum_{j=1}^n h(x_j) = f(\mathbf{x}). \quad (2.9)$$

■

2.1.3 Other characterisations of majorisation

Another characterisation of majorisation shows that we can focus on processes acting non-trivially only on two-dimensional subsystems at a time. Such elementary processes are called T -transforms ([19], Chapter 2):

Definition 2.8. (T-transforms) Let Π_{ij} be a permutation in $\mathbb{R}^n$ transposing indices i and j . A T -transform is defined as

$$T = \lambda \mathbb{I} + (1 - \lambda) \Pi_{ij}, \quad (2.10)$$

where $\mathbb{I}$ is the identity matrix in $\mathbb{R}^n$ and $\lambda \in [0, 1]$.

Lemma 2.9 (Muirhead, Littlewood, Hardy and Polya). $\mathbf{x} \succ \mathbf{y}$ if and only if there exists a finite sequence $T_1, \dots, T_m$ of T -transforms such that $\mathbf{y} = T_m \dots T_1 \mathbf{x}$.

For completeness, a proof is given in Aside 2.2. As we said before, each Schur-convex (or concave) function captures some aspects of the structure induced by majorisation. Sometimes, however, a whole family of functionals is enough to fully characterise a partial ordering. This is the spirit of the following characterisation of majorisation [20]:

Lemma 2.10. $\mathbf{x} \succ \mathbf{y}$ if and only if

$$\sum_{i=1}^n |x_i - a| \geq \sum_{i=1}^n |y_i - a| \quad \forall a \geq 0. \quad (2.11)$$

Proof. Without loss of generality we assume here $\sum_{i=1}^n x_i = \sum_{i=1}^n y_i = 1$. Define $f_a(\mathbf{x}) = \sum_{i=1}^n |x_i - a|$ and assume Eq. (2.11) holds. Fix $j \in \{1, \dots, n\}$ and define $k \geq 0$ the largest index such that $y_i^\downarrow \geq x_j^\downarrow$ for all $i \leq k$. Now, if k does not exist, then $y_i^\downarrow \leq x_j^\downarrow$ for all $i = 1, \dots, n$. Hence we conclude $\sum_{i=1}^j y_i^\downarrow \leq j x_j^\downarrow \leq \sum_{i=1}^j x_i^\downarrow$. On the other hand, assume $k > 0$ exists. Then, taking $a = x_j^\downarrow$,

$$f_{x_j^\downarrow}(\mathbf{x}) = 2 \sum_{i=1}^j x_i^\downarrow - 1 + (n - 2j) x_j^\downarrow, \quad f_{x_j^\downarrow}(\mathbf{y}) = 2 \sum_{i=1}^k y_i^\downarrow - 1 + (n - 2k) x_j^\downarrow. \quad (2.12)$$

From Eq. (2.11),

$$0 \leq f_{x_j^\downarrow}(\mathbf{x}) - f_{x_j^\downarrow}(\mathbf{y}) = 2 \sum_{i=1}^j x_i^\downarrow - 2 \sum_{i=1}^k y_i^\downarrow + 2(k-j)x_j^\downarrow \leq 2 \sum_{i=1}^j x_i^\downarrow - 2 \sum_{i=1}^j y_i^\downarrow, \quad (2.13)$$

where, regarding the last inequality, we used

1. If $k \geq j$, $-\sum_{i=j+1}^k y_i^\downarrow + (k-j)x_j^\downarrow \leq 0$, as $y_i^\downarrow \geq x_j^\downarrow$ for $i = j+1, \dots, k$.
2. If $k < j$, $\sum_{i=k+1}^j y_i^\downarrow - (j-k)x_j^\downarrow \leq 0$, as $y_i^\downarrow \leq x_j^\downarrow$ for all $i = k+1, \dots, j$.

As j can be taken to be any integer between 1 and $n-1$, this shows that majorisation holds.

Conversely, $f_a(\mathbf{x}) = \sum_i h_a(x_i)$, with $h_a(x) = |x - a|$. For any a , h_a is a convex function on $\mathbb{R}$ due to the triangular inequality. From Aside 2.1, f_a is Schur-convex, so $\mathbf{x} \succ \mathbf{y}$ implies Eq. (2.11). ■

Mathematical Aside 2.2. Proofs of Theorem 2.4 and Lemma 2.9

The following statements are equivalent [20]:

1. $\mathbf{x} \succ \mathbf{y}$,
2. $\mathbf{y}$ can be obtained from $\mathbf{x}$ through a sequence of T -transforms,
3. $\mathbf{y}$ is in the convex hull of permutations of $\mathbf{x}$,
4. $\mathbf{y} = M\mathbf{x}$ for a doubly-stochastic matrix M .

Proof. (1 $\Rightarrow$ 2) If $\mathbf{x}, \mathbf{y} \in \mathbb{R}^2$, then $\mathbf{x} \succ \mathbf{y}$ if and only if $x_1^\downarrow \geq y_1^\downarrow$ and $x_1^\downarrow + x_2^\downarrow = y_1^\downarrow + y_2^\downarrow$. This implies $x_2^\downarrow \leq y_2^\downarrow$, so $x_1^\downarrow \geq y_1^\downarrow \geq y_2^\downarrow \geq x_2^\downarrow$. Hence, $y_1^\downarrow = tx_1^\downarrow + (1-t)x_2^\downarrow$ for some $t \in [0, 1]$. From this and $y_2^\downarrow = x_1^\downarrow + x_2^\downarrow - y_1^\downarrow$, we get $y_2^\downarrow = (1-t)x_1^\downarrow + tx_2^\downarrow$. Hence $\mathbf{y}$ can be obtained from $\mathbf{x}$ by means of a T -transform. We now proceed by induction. Assume the case $n-1$. By means of permutations, assume both $\mathbf{x}$ and $\mathbf{y}$ are sorted in decreasing order (permutations are T -transforms so this is fine). Since $\mathbf{x} \succ \mathbf{y}$, we have $x_1 \geq y_1 \geq x_n$ (the second inequality follows from $x_n \leq y_n \leq y_1$). Let k be the smallest index such that $x_1 \geq y_1 \geq x_k$. Then $y_1 = tx_1 + (1-t)x_k$, $t \in [0, 1]$. Let $\mathbf{z} = T_1\mathbf{x}$, where T_1 is a T -transform such that $z_1 = tx_1 + (1-t)x_k$. As we have seen above for the case of $\mathbb{R}^2$ we must have $z_k = (1-t)x_1 + tx_k$. Note that $z_1 = y_1$. Moreover, denote by $\tilde{\mathbf{z}}$ and $\tilde{\mathbf{y}}$ the vectors $\mathbf{z}$ and $\mathbf{y}$ truncated of the first element. We have

$$\tilde{\mathbf{z}} = (x_2, \dots, x_{k-1}, (1-t)x_1 + tx_k, x_{k+1}, \dots, x_n). \quad (2.14)$$

By definition of k , $x_1 \geq \dots \geq x_{k-1} \geq y_1 \geq \dots \geq y_n$. It follows that $\sum_{i=2}^m x_i \geq \sum_{i=2}^m y_i$ for all $m = 2, \dots, k-1$. For $m \geq k$, due to $\mathbf{x} \succ \mathbf{y}$,

$$\sum_{i=2}^m \tilde{z}_i = \sum_{i=2}^{k-1} x_i + (1-t)x_1 + tx_k + \sum_{i=k+1}^m x_i = \sum_{i=1}^m x_i - tx_1 + (t-1)x_k \geq \sum_{i=1}^m y_i - y_1 = \sum_{i=2}^m \tilde{y}_i.$$

Equality holds when $m = n$ because $\mathbf{x} \succ \mathbf{y}$. We conclude that $\tilde{\mathbf{z}} \succ \tilde{\mathbf{y}}$. By induction hypothesis, there is a set of T -transforms $T_2, \dots, T_p$ such that $T_p \dots T_2 \tilde{\mathbf{z}} = \tilde{\mathbf{y}}$. Hence, $T_p \dots T_2 T_1 \mathbf{x} = \mathbf{y}$. (2 $\Rightarrow$ 3) Each T -transform is a convex combination of the identity and a transposition. Hence, the composition of T -transforms is a convex combination of permutations, from which the statement follows. (3 $\Rightarrow$ 4) A convex combination of permutations is a doubly stochastic matrix. (4 $\Rightarrow$ 5) Without loss of generality, assume $\mathbf{x}, \mathbf{y}$ are sorted in non-increasing order. Fix $k \in \{1, \dots, n\}$. By assumption $y_j = \sum_{i=1}^n M_{j|i} x_i$. Then $\sum_{j=1}^k y_j = \sum_{i=1}^n t_i x_i$, where we defined $t_i = \sum_{j=1}^k M_{j|i} \in [0, 1]$. Moreover, $\sum_{i=1}^n t_i = k$. Then,

$$\begin{aligned} \sum_{i=1}^n t_i x_i - \sum_{i=1}^k x_i &= \sum_{i=1}^k (t_i - 1) x_i + \sum_{i=k+1}^n t_i x_i - \left(k - \sum_{i=1}^k t_i \right) x_k = \\ \sum_{i=1}^k (t_i - 1)(x_i - x_k) &+ \sum_{i=k+1}^n t_i (x_i - x_k) \leq 0. \end{aligned}$$

So $\sum_{j=1}^k y_j \leq \sum_{j=1}^k x_j$, and equality holds for $k = n$ because M is doubly-stochastic. We conclude that $\mathbf{x} \succ \mathbf{y}$. ■

2.1.4 Ordering states in thermodynamics: thermo-majorisation

We have seen that majorisation is equivalent to the existence of stochastic processes having the uniform distribution as a fixed point of the dynamics. In thermodynamics, we are typically interested in thermalisation processes. A necessary condition for a process to lead to thermal equilibrium is that the thermal state is a fixed point of the dynamics. It is then natural to look for a generalisation of majorisation satisfying Theorem 2.4 for such processes. This leads to the concept of thermo-majorisation. Given a Hamiltonian H with discrete spectrum $\{E_i\}$, we define the distribution $\mathbf{g}$ as

$$g_i = \frac{e^{-\beta E_i}}{Z_H}, \quad Z_H = \sum_{i=1}^n e^{-\beta E_i}. \quad (2.15)$$

This is the thermal equilibrium state of a system with Hamiltonian H , in the presence of a surrounding environment at temperature T_B , where $\beta = (kT_B)^{-1}$ and k is the Boltzmann constant.

Definition 2.11. We say that $\mathbf{x}$ thermo-majorises $\mathbf{y}$ with respect to $\mathbf{g}$, and write $\mathbf{x} \succ_g \mathbf{y}$, if and only if there exist a stochastic matrix M satisfying

$$M\mathbf{x} = \mathbf{y}, \quad M\mathbf{g} = \mathbf{g}. \quad (2.16)$$

We define the set of stochastic matrices satisfying Eq. (2.16) as *Gibbs-preserving stochastic processes*, and denote them by $\mathcal{G}$. We could just present the condition for existence of a stochastic matrix M satisfying Eq. (2.16). We prefer instead to give an elementary and

self-contained exposition and save the reader the quest of digging in specialised mathematical journals (see [21, 22] and references therein).

The basic tool here will be the embedding map introduced in [23]. Assume the thermal state $\mathbf{g}$ is a vector of rational numbers, i.e. there exists $d_1, \dots, d_n \in \mathbb{N}$:

$$\mathbf{g} = \left(\frac{d_1}{D}, \dots, \frac{d_n}{D} \right), \quad (2.17)$$

where $D := \sum_{i=1}^n d_i$. Of course, any irrational $\mathbf{g}$ can be approximated to an arbitrary precision as in Eq. (2.17). Then, if $\mathbf{d} := (d_1, \dots, d_n)$, we define

Definition 2.12 (Embedding map). $\Gamma_{\mathbf{d}} : \mathbb{R}^n \rightarrow \mathbb{R}^D$ is the function

$$\Gamma_{\mathbf{d}}(\mathbf{x}) = \left(\underbrace{\frac{x_1}{d_1}, \dots, \frac{x_1}{d_1}}_{d_1\text{-times}}, \dots, \underbrace{\frac{x_n}{d_n}, \dots, \frac{x_n}{d_n}}_{d_n\text{-times}} \right) := \oplus_i x_i \boldsymbol{\eta}_i, \quad (2.18)$$

with $\boldsymbol{\eta}_i$ a d_i -dimensional uniform distribution.

By definition, $\Gamma_{\mathbf{d}}(\mathbf{g}) = \boldsymbol{\eta}_D$, where $\boldsymbol{\eta}_D$ is the D -dimensional uniform distribution. The (left) inverse of $\Gamma_{\mathbf{d}}$ is the map $\Gamma_{\mathbf{d}}^{-1} : \mathbb{R}^D \rightarrow \mathbb{R}^n$ defined by

$$\Gamma_{\mathbf{d}}^{-1}(\mathbf{p}) = \mathbf{x}, \quad (2.19)$$

where $x_i = \sum_{j=j_{i-1}+1}^{j_i} p_j$, $j_i = \sum_{k=0}^i d_k$ and $d_0 := 0$, for $i = 1, \dots, n$. This simply amounts to taking the various blocks on the right-hand side of Eq. (2.12) and summing over the elements within each block. Then, $\Gamma_{\mathbf{d}}^{-1}(\Gamma_{\mathbf{d}}(\mathbf{x})) = \mathbf{x}$ for all $\mathbf{x} \in \mathbb{R}^n$ (but, conversely, $\Gamma_{\mathbf{d}}(\Gamma_{\mathbf{d}}^{-1}(\mathbf{x}))$ is not the identity on $\mathbb{R}^D$).

The embedding is a bridge between thermo-majorisation and majorisation, as the following lemma shows:

Lemma 2.13. $\mathbf{x} \succ_g \mathbf{y}$ if and only if $\Gamma_{\mathbf{d}}(\mathbf{x}) \succ \Gamma_{\mathbf{d}}(\mathbf{y})$.

Proof. By definition, $\mathbf{x} \succ_g \mathbf{y}$ if and only if there exists M stochastic such that $M\mathbf{x} = \mathbf{y}$ and $M\mathbf{g} = \mathbf{g}$. Let $\tilde{M} = \Gamma_{\mathbf{d}} \circ M \circ \Gamma_{\mathbf{d}}^{-1}$. $\tilde{M}$ is stochastic, because it is a composition of stochastic matrices. Moreover, it is easy to check that $\tilde{M}\boldsymbol{\eta}_D = \boldsymbol{\eta}_D$ and $\tilde{M}(\Gamma_{\mathbf{d}}(\mathbf{x})) = \Gamma_{\mathbf{d}}(\mathbf{y})$. Using Theorem 2.4, the result follows. ■

In the same way in which we defined Schur-concave functions as those preserving the majorisation ordering, we can define functions that preserve the thermo-majorisation ordering. In the absence of a generally agreed name for such functions, we call them thermodynamic Schur-concave functions (or $\mathbf{g}$ -Schur-concave functions for short):

Definition 2.14. A function $f : \mathbb{R}^n \rightarrow \mathbb{R}$ is called $\mathbf{g}$ -Schur-convex (respectively, $\mathbf{g}$ -Schur-concave) if and only if

$$\mathbf{x} \succ_g \mathbf{y} \Rightarrow f(\mathbf{x}) \geq f(\mathbf{y}) \quad (\text{respectively, } f(\mathbf{x}) \leq f(\mathbf{y})). \quad (2.20)$$

If Schur-concave functions are akin to entropies, thermodynamic Schur-convex functions are akin to free energies, each capturing some aspect of the ordering.

Mathematical Aside 2.3. Thermodynamic Schur-concave functions toolbox

As before, we can give a tool to construct g -Schur-concave functions on $(\mathbb{R}^n, \succ)$ from concave functions on $\mathbb{R}$: Let $h : \mathbb{R} \rightarrow \mathbb{R}$ be concave (convex). Then the function f

$$f(\mathbf{x}) = \sum_{i=1}^n g_i h\left(\frac{x_i}{g_i}\right), \quad (2.21)$$

is g -Schur-concave (g -Schur-convex).

Proof. We prove the statement for h convex (the other case is the same). From Def. 2.11, $\mathbf{x} \succ_g \mathbf{y}$ if and only if $y_i = \sum_{j=1}^n M_{i|j} x_j$, with $\sum_{j=1}^n M_{i|j} \frac{g_j}{g_i} = 1$ and $\sum_{i=1}^n M_{i|j} = 1$. Then,

$$f(\mathbf{y}) = \sum_{i=1}^n g_i h\left(\sum_{j=1}^n M_{i|j} \frac{x_j}{g_i}\right) = \sum_{i=1}^n g_i h\left(\sum_{j=1}^n \left[M_{i|j} \frac{g_j}{g_i}\right] \frac{x_j}{g_j}\right) \leq \sum_{j=1}^n g_j h\left(\frac{x_j}{g_j}\right) = f(\mathbf{x}).$$

■

Following the same discussion given for majorisation, one can argue that thermo-majorisation is a more refined concept than the standard constraint of decreasing free energy. This can be seen as follows. Define $F(\mathbf{x}) = U(\mathbf{x}) - kT_B H(\mathbf{x})$, where $U(\mathbf{x}) = \sum_i x_i E_i$ is the average energy. Because $x \log x$ is convex, $F(\mathbf{x})$ is g -Schur-convex (see Aside 2.3). Hence, if there exists a process with the thermal state as a fixed point transforming $\mathbf{x}$ into $\mathbf{y}$, i.e. if $\mathbf{x} \succ_g \mathbf{y}$, we must have $F(\mathbf{x}) \geq F(\mathbf{y})$. However, as we will later show, the decrease of the free energy F does *not* guarantee the existence of such physical process.

Similarly to the case of majorisation (with Eq. (2.11)), there are families of functionals that completely capture the thermo-majorisation ordering:

Lemma 2.15. $\mathbf{x} \succ_g \mathbf{y}$ if and only if

$$\sum_{i=1}^n |x_i - ag_i| \geq \sum_{i=1}^n |y_i - ag_i| \quad \forall a \geq 0. \quad (2.22)$$

Proof. From Lemma 2.10, $\Gamma_d(\mathbf{x}) \succ \Gamma_d(\mathbf{y})$ if and only if

$$\sum_{i=1}^D |\Gamma_d(\mathbf{x})_i - a| \geq \sum_{i=1}^D |\Gamma_d(\mathbf{y})_i - a| \quad \forall a \geq 0, \quad (2.23)$$

where $D = \sum_{i=1}^n d_i$. Define $j_k = \sum_{i=0}^k d_i$, where $d_0 := 0$. Then,

$$\sum_{i=1}^D |\Gamma_d(\mathbf{x})_i - a| = \sum_{k=1}^n \sum_{i=j_{k-1}+1}^{j_k} \left| \frac{x_k}{d_k} - a \right| = \sum_{k=1}^n d_k \left| \frac{x_k}{d_k} - a \right| = \sum_{k=1}^n |x_k - ad_k|. \quad (2.24)$$

Using $d_k = Dg_k$ and absorbing a constant D in a , we find $\Gamma_d(\mathbf{x}) \succ \Gamma_d(\mathbf{y})$ if and only if Eq. (2.22) holds. We conclude using Lemma 2.13. $\blacksquare$

Discussing majorisation, we started from a well-known definition of a partial ordering among vectors (Def. 2.1) and analysed its operational meaning. On the other hand, we decided to define thermo-majorisation operationally (Def. 2.11) and explore the consequences from there. So we close the circle showing that Def. 2.11 is equivalent to a relation among real vectors that is a natural generalisation of Def. 2.1. It is simpler to introduce this problem in the geometrical form. Let $x_i^{\downarrow\beta}$ be the so-called β -ordering [24], defined as the rearrangement of the indices i that ensures that the vector x_i/g_i is sorted in non-increasing order.⁵ For simplicity, we give the definition for probability distributions:

Definition 2.16 (Thermo-majorisation curves). Let $T(\mathbf{x})$ be the piecewise linear curve in $\mathbb{R}^2$ obtained by joining the origin and the points $(\sum_{i=1}^k g_i^{\downarrow\beta}, \sum_{i=1}^k x_i^{\downarrow\beta})$, for $k = 1, \dots, n$ (where g_i are sorted according to the β -ordering given by $\mathbf{x}$). We say that $T(\mathbf{x}) \succ T(\mathbf{y})$ if and only if the curve $T(\mathbf{x})$ lies all above $T(\mathbf{y})$.

Lemma 2.17. $\mathbf{x} \succ_g \mathbf{y}$ if and only if $T(\mathbf{x}) \succ T(\mathbf{y})$.

Proof. The equivalence can be seen using Lemma 2.13. Sorting in decreasing order the D -dimensional probability distributions $\Gamma_d(\mathbf{x})$ and $\Gamma_d(\mathbf{y})$ corresponds to β -ordering the n -dimensional probability distributions $\mathbf{x}$ and $\mathbf{y}$. Then we can use that $\Gamma_d(\mathbf{x}) \succ \Gamma_d(\mathbf{y})$ if and only if $L(\Gamma_d(\mathbf{x})) \succ L(\Gamma_d(\mathbf{y}))$. If we remove from the points used to construct $L(\Gamma_d(\mathbf{x}))$ all the non-extremal points that lie on a segment of given slope, we obtain the same Lorenz curve. In particular, instead of joining all points $(k, \sum_{i=1}^k (x_i/d_i)^{\downarrow})$, $k = 1, \dots, D$, we can just join the points at the “elbows”; i.e., define $k_s = \sum_{i=1}^s d_i^{\downarrow\beta}$ and join $(k_s, \sum_{i=1}^{k_s} \Gamma_d^{\downarrow}(\mathbf{x})_i)$, $s = 1, \dots, n$ (as well as the origin). But $(k_s, \sum_{i=1}^{k_s} \Gamma_d^{\downarrow}(\mathbf{x})_i) = (D \sum_{i=1}^s g_i^{\downarrow\beta}, \sum_{i=1}^s x_i^{\downarrow\beta})$, which is the same as $T(\mathbf{x})$ apart for a rescaling of the x -axis. Of course this rescaling, being the same for all curves, does not affect the comparison, so we conclude $L(\Gamma_d(\mathbf{x})) \succ L(\Gamma_d(\mathbf{y}))$ if and only if $T(\mathbf{x}) \succ T(\mathbf{y})$, which concludes the proof. $\blacksquare$

The curves $T(\mathbf{x})$ are called *thermo-majorisation curves*. They offer a relatively simple set of constraints equivalent to the existence of a physical process transforming a state $\mathbf{x}$ into a state $\mathbf{y}$, while leaving the thermal state unchanged:

$$\exists M \in \mathcal{G} : M\mathbf{x} = \mathbf{y} \quad \Leftrightarrow \quad T(\mathbf{x}) \succ T(\mathbf{y}). \quad (2.25)$$

As promised, we give an example of a transformation that is provably impossible, even if the free energy goes down:

⁵If $x_i/g_i = x_j/g_j$ for two distinct indices i and j , i precedes j in the β -ordering if $x_i \geq x_j$. This ensures we recover majorisation in the ∞ -temperature limit $\beta \rightarrow 0$.

Example 2.18. Consider the Hamiltonian with spectrum $E_0 = 0$, $E_1 = 1$, $E_2 = 2$ and let $\beta = 1.2$. Hence, $\mathbf{g} = (0.718436, 0.216389, 0.0651751)$. Let $\mathbf{x} = (1/3, 1/3, 1/3)$ and $\mathbf{y} = (2/3, 1/3, 0)$. Then $F(\mathbf{x}) \approx 0.084 > F(\mathbf{y}) \approx -0.197$. Nevertheless, $T(\mathbf{x})$ crosses $T(\mathbf{y})$, so there is no map transforming $\mathbf{x}$ into $\mathbf{y}$ while leaving $\mathbf{g}$ fixed. To see this, notice that $\mathbf{x}^{\downarrow\beta} = (x_3, x_2, x_1)$ and $\mathbf{y}^{\downarrow\beta} = (y_2, y_1, y_3)$. So, to obtain $T(\mathbf{x})$ we need to join $\{(0, 0), (0.0651751, 1/3), (0.281564, 2/3), (1, 1)\}$; and to get $T(\mathbf{y})$ we need to join $\{(0, 0), (0.216389, 1/3), (0.934816, 1), (1, 1)\}$ (see Fig. 2.5).

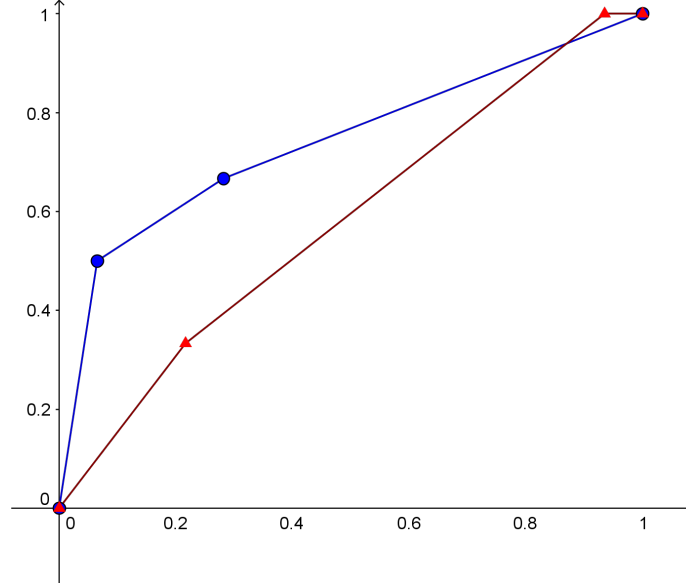


Figure 2.5. Thermo-majorisation curves vs free energy. The thermo-majorisation curves of $\mathbf{x}$ and $\mathbf{y}$ from Example 2.18, denoted by $T(\mathbf{x})$ and $T(\mathbf{y})$, respectively. $T(\mathbf{x})$ is the curve connecting the blue dots, whereas $T(\mathbf{y})$ is obtained connecting the red triangles. Despite $F(\mathbf{x}) > F(\mathbf{y})$, $T(\mathbf{x})$ does not lie all above $T(\mathbf{y})$. Hence, there is no stochastic process M with $M\mathbf{g} = \mathbf{g}$ and $M\mathbf{x} = \mathbf{y}$ ($\mathbf{g}$ here is the Gibbs distribution).

2.1.5 Catalysis

Catalysis is a phenomenon in which a transformation $A \rightarrow B$ is impossible (or very inefficient), but one can perform $A + C \rightarrow B + C$, where an auxiliary state C (a “catalyst”) aids the transition but is given back unchanged at the end of the process.

In the context of majorisation this is formalised by the existence of probability distributions such that $\mathbf{x} \not\succ \mathbf{y}$, but $\mathbf{x} \otimes \mathbf{c} \succ \mathbf{y} \otimes \mathbf{c}$ for some appropriate $\mathbf{c}$:

Definition 2.19. (Catalytic majorisation) We say that $\mathbf{x}$ catalytically majorises $\mathbf{y}$ (or $\mathbf{x}$ trumps $\mathbf{y}$) if and only if there exists $\mathbf{c}$ such that

$$\mathbf{x} \otimes \mathbf{c} \succ \mathbf{y} \otimes \mathbf{c}. \quad (2.26)$$

This will be denoted as $\mathbf{x} \succ^{cat} \mathbf{y}$.

Example 2.20. Consider the probabilities $\mathbf{x} = (0.5, 0.25, 0.25, 0)$, $\mathbf{y} = (0.4, 0.4, 0.1, 0.1)$, $\mathbf{c} = (0.6, 0.4)$ [25]. One can easily verify that $\mathbf{x} \not\succ \mathbf{y}$. However, $\mathbf{x} \otimes \mathbf{c} \succ \mathbf{y} \otimes \mathbf{c}$. Applications to the theory of bipartite, pure state entanglement follow from Nielsen's theorem [26].

Some conditions are necessary for catalysis to occur. For example, the Shannon entropy being additive on independent variables, means that a necessary condition is $H(\mathbf{x}) \leq H(\mathbf{y})$. In fact, reasoning in the same way, if f is any Schur-concave additive function then it is necessary that $f(\mathbf{x}) \leq f(\mathbf{y})$ for Eq. (2.26) to be satisfied. Conversely, one may wonder if the monotonicity of every Schur-concave additive function is a sufficient condition for catalysis to occur. Going even further, is there some family of Schur-concave additive functions that gives sufficient conditions for (2.26)? An affirmative answer was given, based on the notion of Rényi entropies:

Definition 2.21 (Rényi entropies [27] and Burg entropy). The *Rényi entropy* of order α is defined as:

$$H_\alpha(\mathbf{x}) = \frac{\text{sgn}(\alpha)}{1 - \alpha} \log \sum_{i=1}^n x_i^\alpha.$$

The cases $\alpha \in \{-\infty, 0, 1, +\infty\}$ are defined by appropriate limits. Denoting by H the Shannon entropy and by $\text{rank}(\mathbf{x})$ the number of non-zero elements in $\mathbf{x}$,

$$\begin{aligned} H_\infty(\mathbf{x}) &= -\log \max_i x_i, & H_1(\mathbf{x}) &= -\sum_i x_i \log x_i \equiv H(\mathbf{x}), \\ H_0(\mathbf{x}) &= \log \text{rank}(\mathbf{x}), & H_{-\infty}(\mathbf{x}) &= \log \min_i x_i. \end{aligned}$$

The *Burg entropy* is defined as

$$H_{\text{Burg}}(\mathbf{x}) = \frac{1}{d} \sum_i \ln x_i. \quad (2.27)$$

There is hierarchy among entropies, in the sense that $\alpha_1 \geq \alpha_2 \Rightarrow H_{\alpha_1}(\mathbf{x}) \leq H_{\alpha_2}(\mathbf{x})$ for any probability vector $\mathbf{x}$. Recall that $\mathbf{x}^\downarrow$ denotes the vector $\mathbf{x}$ sorted in non-increasing order. We then have

Theorem 2.22 (Turgut [28], Klimesh [29]). *Given $\mathbf{x}$ and $\mathbf{y}$ with $\mathbf{x}^\downarrow \neq \mathbf{y}^\downarrow$ and such that at least one of $\mathbf{x}, \mathbf{y}$ contains no zeroes, we have*

$$\mathbf{x} \succ^{\text{cat}} \mathbf{y} \Leftrightarrow \begin{cases} H_\alpha(\mathbf{x}) < H_\alpha(\mathbf{y}), & \forall \alpha \in \mathbb{R}, \\ H_{\text{Burg}}(\mathbf{x}) < H_{\text{Burg}}(\mathbf{y}). \end{cases} \quad (2.28)$$

The proof is very lengthy and technical and it is hence omitted. This result was slightly improved upon in [23], where less rigid conditions are obtained by changing the problem into finding an arbitrarily good approximation of a trumped state. The proof is presented in Aside 2.4.

Theorem 2.23 (Turgut, Klimesh, Brandao *et al.* [23, 28, 29]). *Given $\mathbf{x}$, for every $\epsilon > 0$ there*

exists $\mathbf{y}_\epsilon$ such that

$$\mathbf{x} \succ^{cat} \mathbf{y}_\epsilon, \quad \|\mathbf{y}_\epsilon - \mathbf{y}\| \leq \epsilon, \quad (2.29)$$

if and only if $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y})$, $\forall \alpha \in \mathbb{R}$.

Mathematical Aside 2.4. Proof of Theorem 2.23

The map $x \mapsto x^\alpha$ on $\mathbb{R}^+$ is strictly convex for $\alpha > 1$ and $\alpha < 0$, whereas it is strictly concave for $\alpha \in (0, 1)$. Hence, from Aside 2.1, $\sum_i x_i^\alpha$ is strictly Schur-convex for $\alpha > 1$ and $\alpha < 0$ and strictly Schur-concave in $\alpha \in (0, 1)$. Because $\text{sgn}(\alpha)/(1 - \alpha) < 0$ for $\alpha > 1$ and $\alpha < 0$, H_α is *strictly* Schur-concave for all $\alpha \in \mathbb{R}$ (note that the limiting cases should be checked separately). A similar argument on the function $x \mapsto \log x$ shows that the Burg entropy is strictly Schur-concave.

Assume first that Eq. (2.29) holds. For any $\epsilon > 0$, since H_α is Schur-concave and additive on independent probability distributions, $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y}_\epsilon)$. Taking the limit $\epsilon \rightarrow 0$ one finds, by continuity, $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y})$.

Conversely, assume $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y})$ for all $\alpha \in \mathbb{R}$. The satisfaction of these condition implies $H_{Burg}(\mathbf{x}) \leq H_{Burg}(\mathbf{y})$. In fact, if $\mathbf{x}$ is not full rank, $H_{Burg}(\mathbf{x}) = -\infty$, so the condition is automatically satisfied. And if $\mathbf{y}$ is not full rank, the conditions $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y})$ for all $\alpha \in \mathbb{R}$ imply, looking at $\alpha < 0$, that $\mathbf{x}$ is also not full rank. But then $H_{Burg}(\mathbf{x}) = H_{Burg}(\mathbf{y}) = -\infty$. Finally, if $\mathbf{x}$ and $\mathbf{y}$ are both full rank, we can use [23]

$$\lim_{\alpha \rightarrow 0^+} \frac{1 - \alpha}{\alpha} (\log n - H_\alpha(\mathbf{x})) = -H_{Burg}(\mathbf{x}) - \log d. \quad (2.30)$$

So, by continuity, $H_\alpha(\mathbf{x}) \leq H_\alpha(\mathbf{y})$ for all $\alpha \in \mathbb{R}$ implies $H_{Burg}(\mathbf{x}) \leq H_{Burg}(\mathbf{y})$.

Define $\mathbf{y}_\epsilon := (1 - \delta_\epsilon)\mathbf{y} + \delta_\epsilon\boldsymbol{\eta}$, where $\boldsymbol{\eta}$ is the uniform distribution and $\delta_\epsilon > 0$ is chosen small enough so that $\|\mathbf{y}_\epsilon - \mathbf{y}\| < \epsilon$. $\mathbf{y}_\epsilon$ is obtained from $\mathbf{y}$ by means of a bistochastic map. Because H_α is strictly Schur-concave, $H_\alpha(\mathbf{y}) < H_\alpha(\mathbf{y}_\epsilon)$ and so $H_\alpha(\mathbf{x}) < H_\alpha(\mathbf{y}_\epsilon)$. Moreover, $H_{Burg}(\mathbf{x}) \leq H_{Burg}(\mathbf{y}) < H_{Burg}(\mathbf{y}_\epsilon)$. We are then in the conditions of Theorem 2.22 (that we can use because $\mathbf{y}_\epsilon$ does not have any zeros). It follows that, for any $\epsilon > 0$, $\mathbf{x} \succ^{cat} \mathbf{y}_\epsilon$.

It should not come as a surprise by now that this result can be generalised to the thermo-majorisation ordering.

Definition 2.24 (Catalytic thermo-majorisation). We say that $\mathbf{x}$ catalytically thermo-majorises $\mathbf{y}$ if and only if there exists $\mathbf{c}$ such that

$$\mathbf{x} \otimes \mathbf{c} \succ_g \mathbf{y} \otimes \mathbf{c}. \quad (2.31)$$

This will be denoted as $\mathbf{x} \succ_g^{cat} \mathbf{y}$.

Using the embedding map (Def. 2.12), Rényi entropies naturally lead to the definition of α -free energies of [23] (see Aside 2.5). Recall that $g_i = e^{-\beta E_i}/Z_H$. Then,

Definition 2.25. The α -free energy of $\mathbf{p}$ is defined as

$$F_\alpha(\mathbf{p}) = -kT_B \log Z_H + kT_B S_\alpha(\mathbf{p}||\mathbf{g}), \quad (2.32)$$

where S_α are the so-called α -Rényi divergences, defined for $\alpha \in \mathbb{R} \setminus \{0, 1\}$ as [27]

$$S_\alpha(\mathbf{p}||\mathbf{q}) = \frac{\text{sgn}(\alpha)}{\alpha - 1} \log \sum_i p_i^\alpha q_i^{1-\alpha}. \quad (2.33)$$

The cases $\alpha \in \{-\infty, 0, 1, +\infty\}$ are defined via suitable limits (see e.g. [23]):

$$S_\infty(\mathbf{x}||\mathbf{g}) = \log \max_i x_i/g_i, \quad S_1(\mathbf{x}||\mathbf{g}) = \sum_i x_i \log(x_i/g_i),$$

$$S_0(\mathbf{x}||\mathbf{g}) = -\log \sum_{i|x_i \neq 0} g_i, \quad S_{-\infty}(\mathbf{x}||\mathbf{g}) = S_\infty(\mathbf{g}||\mathbf{x}).$$

In particular notice that $F_1(\mathbf{x}) = F(\mathbf{x})$, as defined above.

Mathematical Aside 2.5. Embedding Rényi entropies gives α -free energies

$H_\alpha(\Gamma_{\mathbf{d}}(\mathbf{x}))$ is equal to $F_\alpha(\mathbf{x})$, modulo affine transformations.

Proof. Define $d_0 = 0$, $j_k = \sum_{i=0}^k d_i$. Then

$$H_\alpha(\Gamma_{\mathbf{d}}(\mathbf{x})) = \frac{\text{sgn}(\alpha)}{1 - \alpha} \log \sum_{k=1}^n \sum_{i=j_{k-1}+1}^{j_k} \Gamma_{\mathbf{d}}(\mathbf{p})_i^\alpha = \frac{\text{sgn}(\alpha)}{1 - \alpha} \log \sum_{k=1}^n \frac{x_k^\alpha}{d_k^{\alpha-1}} \quad (2.34)$$

Using $d_i = g_i D$ and performing an affine transformation (with negative constant) we obtain Eq. (2.32). ■

Theorem 2.26 (Brandao *et al.* [23]). *For every $\epsilon > 0$ there exists $\mathbf{y}_\epsilon$ such that*

$$\mathbf{x} \succ_g^{\text{cat}} \mathbf{y}_\epsilon \quad \|\mathbf{y}_\epsilon - \mathbf{y}\| < \epsilon, \quad (2.35)$$

if and only if $F_\alpha(\mathbf{x}) \leq F_\alpha(\mathbf{y})$, for all $\alpha \in \mathbb{R}$. Moreover, the Hamiltonian of the catalyst can be chosen to be the identity.

Proof. This is a corollary of Theorem 2.23. Assume $F_\alpha(\mathbf{x}) \geq F_\alpha(\mathbf{y})$ for all $\alpha \in \mathbb{R}$. Let $\Gamma_{\mathbf{d}}$ the embedding map transforming $\mathbf{g}$, the thermal state of the system, into a uniform state η_D . The free energy conditions are equivalent to $H_\alpha(\Gamma_{\mathbf{d}}(\mathbf{x})) \leq H_\alpha(\Gamma_{\mathbf{d}}(\mathbf{y}))$ for all $\alpha \in \mathbb{R}$ (due to Aside 2.5). From Theorem 2.23 and the characterisation of majorisation given in Theorem 2.4, this is equivalent to the following: for all $\epsilon > 0$ there exists a map Λ_ϵ and a catalyst $\mathbf{a}_\epsilon$ such that

$$\Lambda_\epsilon(\Gamma_{\mathbf{d}}(\mathbf{x}) \otimes \mathbf{a}_\epsilon) = \Gamma_{\mathbf{d}}(\mathbf{y})_\epsilon \otimes \mathbf{a}_\epsilon, \quad \Lambda_\epsilon(\eta_D \otimes \eta_{\text{cat}}) = \eta_D \otimes \eta_{\text{cat}}, \quad (2.36)$$

where η_{cat} is a uniform distribution on the space of the catalyst and $\Gamma_d(\mathbf{y})_\epsilon \rightarrow \Gamma_d(\mathbf{y})$ as $\epsilon \rightarrow 0$. Now, define $\mathbf{y}_\epsilon = \Gamma_d^{-1}[\Gamma_d(\mathbf{y})_\epsilon]$ and notice that, by continuity, $\mathbf{y}_\epsilon \rightarrow \mathbf{y}$ as $\epsilon \rightarrow 0$. Let $\tilde{\Lambda}_\epsilon := (\Gamma_d^{-1} \otimes \mathbb{I}) \circ \Lambda_\epsilon \circ (\Gamma_d \otimes \mathbb{I})$, where the identity acts on the catalyst space. Then,

$$\tilde{\Lambda}_\epsilon(\mathbf{x} \otimes \mathbf{a}_\epsilon) = \mathbf{y}_\epsilon \otimes \mathbf{a}_\epsilon, \quad \tilde{\Lambda}_\epsilon(\mathbf{g} \otimes \eta_{\text{cat}}) = \mathbf{g} \otimes \eta_{\text{cat}}. \quad (2.37)$$

From Def. 2.11, this shows Eq. (2.35), with the catalyst chosen to have a trivial Hamiltonian. ■

2.2 Resource theories

2.2.1 A quick introduction to the idea of resource theories

Fundamental laws of Nature often take the form of restrictions: nothing can move faster than light in vacuum, energy cannot be created from nothing, there are no perpetual mobiles. It is due to these limitations that we can ascribe value to different objects and phenomena, e.g., energy would not be treated as a resource if we could create it for free. The mathematical framework developed to study the influence of such constraints on the possible evolution of physical systems is known under the collective name of resource theories.

Perhaps the best known example of this approach was to formalize and harness the puzzling phenomenon of quantum entanglement (see [30] and references therein). However, the basic machinery developed to study entanglement is also perfectly suited to shed light on a much older subject – thermodynamics. The first and second laws are fundamental constraints in thermodynamics. These force thermodynamic processes to conserve the overall energy and forbid free conversion of thermal energy into work. Thus, a natural question to ask is: what amounts to a resource when we are restricted by these laws?

These questions can be made precise and addressed within the framework of resource theories. For the scope of the present work, we define a resource theory in the following way:

Definition 2.27. (Resource Theory) A resource theory is defined by

1. A set of *allowed operations*: a subset $\mathcal{F}$ of all quantum operations, closed under composition and typically convex.
2. A set of *free states*: a subset $\mathcal{P}$ of the set of quantum states $\mathcal{D}$. All states in $\mathcal{D} \setminus \mathcal{P}$ are called *resource states*.

Example 2.28. (Theory of entanglement) Consider the following limitations: given n -parties, at each location any preparation is allowed and any amount of randomness can be shared with other parties. Moreover, any party can perform a general quantum operation in its own laboratory and communicate classically with the others. So the free states

are the set of separable states and the free operations are Local Operations and Classical Communication (LOCC). This is known as the resource theory of entanglement.

Of course, the concept of resource theory is much wider than the definition that we gave. We do not enter into details, but one example will hopefully clarify this:

Example 2.29. (Theory of ruler and compass constructions [31]) The space of states is the set of all geometrical figures on paper. The allowed operations are drawing with a pencil using ruler (a straightedge) and compass. Given an angle, you can construct an angle which is half of the initial one (i.e. you can bisect). Impossible transformations include trisections and squaring a circle.

Because preparations of quantum states can be seen as quantum operations themselves, we will just talk of allowed operations $\mathcal{F}$. Define

Definition 2.30. Given a set of free operations $\mathcal{F}$, we write $\rho \succ_{\mathcal{F}} \sigma$ if and only if there exists $\mathcal{E} \in \mathcal{F}$ such that $\mathcal{E}(\rho) = \sigma$.

The relation $\succ_{\mathcal{F}}$ defines a partial ordering on the set of states, once we identify all states that can be reversibly converted into each other. Let us denote by $\mathcal{D}$ the set of all density operations (modulo the above equivalence relation). Similarly to what we have seen in Sec. 2.1, we can define homomorphisms from the partially ordered set $(\mathcal{D}, \succ_{\mathcal{F}})$ to $\mathbb{R}$. In the case of majorisation on probability vectors, this corresponds to Schur-concave functions. In the context of resource theories, these are known under the name of *monotones*:

Definition 2.31. (Monotones) Given a resource theory, a monotone M is a functional $M : (\mathcal{D}, \succ_{\mathcal{F}}) \rightarrow \mathbb{R}$ such that

$$\rho \succ_{\mathcal{F}} \sigma \Rightarrow M(\rho) \geq M(\sigma) \quad (2.38)$$

Monotones allow us to quantify how valuable a resource state is, or at least an aspect of it.

Example 2.32. Consider the resource theory of bipartite entanglement. Define $E(\rho_{AB}) = S(\text{Tr}_B[\rho_{AB}])$, with $S(\rho) = -\text{Tr}[\rho \log \rho]$ the von Neumann entropy. E is known as entanglement entropy. Then if $\mathcal{E} \in \text{LOCC}$, we have $E(\mathcal{E}(\rho_{AB})) \leq E(\rho_{AB})$ [26]. Hence, E is an entanglement monotone.

We now introduce the notion of resource theory for thermodynamics. Moreover, we will introduce another resource theory whose aim is the study of symmetry. The link between the two theories will be clarified in Chapter 4.

2.2.2 The resource theory of Thermal Operations

The resource theory of Thermal Operations was initially defined in [32, 33]. The authors of these works tried to capture the following general setting for thermodynamic transformations. A quantum system, previously isolated and characterized by a Hamiltonian H_S , is brought into thermal contact with a bath described by a Hamiltonian H_B . After

some time the system is decoupled from the bath. The only assumption made is microscopic energy conservation at the level of system plus bath (of course, heat will flow to and from the bath). Formally,

Definition 2.33 (Resource theory of Thermal Operations). It is defined by

1. *Free operations*: partial traces and energy-preserving unitaries;
2. *Free states*: the set of all Gibbs states at a fixed temperature, i.e. $\gamma_B = e^{-\beta H_B} / Z_B$, where $Z_B = \text{Tr} [e^{-\beta H_B}]$, $\beta = (kT_B)^{-1}$ and H_B is an arbitrary Hamiltonian.

Given a state ρ with Hamiltonian H_S , one can combine the previous transformations to obtain the following set of other non-equilibrium states:

$$\mathcal{T}(\rho) = \text{Tr}_B [U(\rho \otimes \gamma_B)U^\dagger], \quad [U, H_S + H_B] = 0. \quad (2.39)$$

The set of quantum operations with the Stinespring dilation of Eq. (2.39) are called *Thermal Operations*.⁶ H_S and H_B should be understood as the non-interacting Hamiltonians of system and bath, and U as the overall effect of an interaction Hamiltonian which is turned on at some time t_i and off at some later time t_f . A property that one can derive from Eq. (2.39) is that Thermal Operations preserve the Gibbs-state:

$$\mathcal{T}(\gamma_S) = \gamma_S, \quad \text{where } \gamma_S = e^{-\beta H_S} / Z_S, \quad Z_S = \text{Tr} [e^{-\beta H_S}]. \quad (2.40)$$

This can be seen as follows, using the overall energy conservation of U :

$$\mathcal{T}(\gamma_S) = \text{Tr}_B \left[U \frac{e^{-\beta(H_S+H_B)}}{Z_S Z_B} U^\dagger \right] = \text{Tr}_B \left[U U^\dagger \frac{e^{-\beta(H_S+H_B)}}{Z_S Z_B} \right] = \frac{e^{-\beta H_S}}{Z_S} = \gamma_S, \quad (2.41)$$

As discussed in the introduction to the idea of resource theory, one can introduce monotones. An important one is the *quantum free energy*:

$$F(\rho) = \text{Tr} [H_S \rho] - kT_B S(\rho). \quad (2.42)$$

Define $\Delta F(\rho) := F(\rho) - F(\gamma_S)$, the free energy difference to the thermal state. Then one has the following well-known result:

Lemma 2.34. $\Delta F(\rho)$ is a monotone under Thermal Operations.

Proof. One can check that $\Delta F(\rho) = kT_B S(\rho || \gamma_S)$, with $S(\rho || \gamma_S) = \text{Tr} [\rho (\log \rho - \log \gamma_S)]$ the quantum relative entropy. Using the contractiveness of relative entropy under quantum operations and Eq. (2.40),

$$\Delta F(\mathcal{T}(\rho)) = kT_B S(\mathcal{T}(\rho) || \gamma_S) = kT_B S(\mathcal{T}(\rho) || \mathcal{T}(\gamma_S)) \leq kT_B S(\rho || \gamma_S) = \Delta F(\rho). \quad (2.43)$$

⁶More generally, one may have different input and output spaces.

The assumptions behind Thermal Operations: a brief discussion

A common misunderstanding about the role of Thermal Operations is the following. These are often compared to frameworks in which a classical field can be applied on the system - as it is often the case in thermodynamic protocols. Compared to such frameworks, Thermal Operations seem unduly limited, especially in their requirement of energy conservation, that may be not satisfied by a thermodynamic protocol as soon as some coupling with a thermal bath is switched on. The crucial point is, however, that Thermal Operations claim to provide a framework for a careful accounting of thermodynamic resources, *not* to set the limits of what can be done in the lab.

In fact, if a resource state σ is available, representing a large enough coherent field and an ancilla initialised in $|0\rangle$, then *every* quantum operation $\mathcal{Q}$ can be approximated on a system ρ using Thermal Operations $\mathcal{T}$ via $\mathcal{Q}(\rho) := \text{Tr}_2 [\mathcal{T}(\rho \otimes \sigma \otimes |0\rangle\langle 0|)]$. The caveat is that, because σ cannot be prepared freely within Thermal Operations (the field is not in a thermal state), an appropriate accounting of its deterioration is necessary [2, 34]. This includes, but is not limited to, an analysis of the energy flows from and to σ . For example, the coherent properties of σ and their deterioration should be investigated. We stress that this is not just a drawback of the resource theory of thermodynamics: it has been extensively discussed in the literature that doing otherwise means using a semiclassical description that is in general not fully satisfactory in small-scale thermodynamics [35–37].

An assumption often made in thermodynamics is to substitute microscopic energy conservation with average energy conservation. This more coarse-grained description can be fine classically, but is unsatisfactory in a number of ways when pushed to “extreme” quantum regimes such as the thermodynamics of a small number of microscopic quantum systems. This is extensively discussed in Chapter 6. To summarise, the study of work fluctuations of small systems and their coherent properties cannot be fully satisfactory within this coarse framework. This is because average energy conservation can hide fluctuations as well as inject coherence from ancillary systems that always stay outside the quantum-mechanical description.

We will often focus our attention on transformations among incoherent states, i.e. states ρ such that $[\rho, H_S] = 0$. In this respect, the following definition is important:

Definition 2.35 (Thermal stochastic processes). Given $\mathcal{T}$ Thermal Operation, define a correspondent stochastic map on the energy eigenbasis $|i\rangle$ as

$$T_{i|j} := \langle i | \mathcal{T}(|j\rangle\langle j|) | i \rangle. \quad (2.44)$$

These stochastic maps will be called *thermal stochastic processes* (or thermal processes, for short). These form a set of stochastic maps that we shall denote by $\mathcal{T}$.⁷

We have the following reduction result for Thermal Operations among incoherent

⁷In general, we should write $T_{i|j} = \text{Tr} [\Pi_i \mathcal{T}(\Pi_j)]$, where Π_i are projectors on the energy eigenspaces.

states:

Proposition 2.36 (Reduction to classical problem). *Let ρ and σ be quantum states with $[\rho, H_S] = [\sigma, H_S] = 0$. Denote by $\mathbf{x}$ and $\mathbf{y}$ the eigenvalues of ρ and σ , respectively. Then there exists a Thermal Operation $\mathcal{T}$ such that $\mathcal{T}(\rho) = \sigma$ if and only if there exists a thermal process $T \in \mathcal{T}$ such that $T\mathbf{x} = \mathbf{y}$.*

Proof. Unitaries U_S on the system satisfying $[U_S, H_S] = 0$ are Thermal Operations. Let $\mathcal{U}_{S,1}(\cdot) = U_{S,1}(\cdot)U_{S,1}^\dagger$ and $\mathcal{U}_{S,2}(\cdot) = U_{S,2}(\cdot)U_{S,2}^\dagger$, where $U_{S,1}, U_{S,2}$ are unitaries diagonalising the energy blocks of ρ and σ , respectively. If $T \in \mathcal{T}$ is such that $T\mathbf{x} = \mathbf{y}$, let $\mathcal{T}$ be a Thermal Operation linked to T by Eq. (2.44) and not rotating the energy eigenspaces. Then $\tilde{\mathcal{T}} = \mathcal{U}_{S,2}^\dagger \circ \mathcal{T} \circ \mathcal{U}_{S,1}$ is a Thermal Operation and satisfies $\tilde{\mathcal{T}}(\rho) = \sigma$. The converse also follows easily. ■

The connection to the theory developed before is made clear by the following result:

Lemma 2.37. *Let $\mathbf{x}$ and $\mathbf{y}$ be two probability distributions. Then the following are equivalent:*

1. *There exists $G \in \mathcal{G}$ such that $G(\mathbf{x}) = \mathbf{y}$.*
2. *There exists $T \in \mathcal{T}$ such that $T(\mathbf{x}) = \mathbf{y}$.*
3. *$\mathbf{x} \succ_g \mathbf{y}$*

Proof. For $1 \Leftrightarrow 3$ see Section 2.1.4. For $2 \Leftrightarrow 3$ see [24, 32]. ■

Using the previous lemma and the reduction Proposition 2.36, we obtain the main result of [24]:

Theorem 2.38. *Let ρ and σ be two incoherent states with eigenvalues $\mathbf{x}$ and $\mathbf{y}$, respectively. Then a Thermal Operation $\mathcal{T}$ mapping ρ into σ exists if and only if $\mathbf{x} \succ_g \mathbf{y}$.*

2.2.3 The resource theory of asymmetry

The idea of symmetry is powerful and wide-reaching, and finds countless applications across physics. However, recent work has brought the concept of asymmetry to the fore, and shown it to be a valuable, consumable resource [38–43]. The broad, conceptual point is the following: a quantum state does not only contain intrinsic information about the system itself, but also extrinsic information about its relation to a (often classical) background reference frame with respect to which the system is described. The same holds true for our description of quantum operations.

The most intuitive example is Cartesian reference frames. A Cartesian reference frame can be understood as a physical object that breaks an underlying symmetry $G = SU(2)$. However, G could be any compact Lie group or even a finite group (say, parity). A classical reference frame is defined, for example, by a token pointing in some direction. One can then measure angles relative to it (of course, only relational quantities have

operational sense). As, ultimately, matter is quantum-mechanical, also quantum systems can be used as such tokens; for example a spin may be used to denote a given direction. Either way, quantum states carry information about extrinsic properties, i.e. their relation to a reference frame with respect to which they are defined.

To make these ideas more precise, we need to speak of the action of a symmetry group on the objects at hand. For example, an arrow is a good token for a direction because, being pointy, it is sensitive to rotations (it is not rotationally symmetric). In quantum mechanics, states are described as elements of a vector space and the action of a symmetry group on them defines a representation of the group.⁸ So, let $g \in G \mapsto U_g$ be a unitary representation of G . Now consider the following operational scenario [38]. Alice and Bob want to exchange information, but they do not share a Cartesian reference frame. In other words, Alice has no idea of how her Cartesian frame is linked to the Cartesian frame in Bob's laboratory and, conversely, Bob has no knowledge about Alice's frame. Say that Alice sends the state ρ to Bob. In Bob's frame, this state is represented as $\mathcal{U}_g(\rho) := U_g \rho U_g^\dagger$, for some $g \in G$. However, Bob has no information about g , so he will average over his ignorance and represent the state that Alice sent him as⁹

$$\mathcal{G}(\rho) = \int_G \mathcal{U}_g(\rho) dg. \quad (2.45)$$

The operation $\mathcal{G}$ is known as *G-twirling*, and corresponds to a group average. Now consider the following definition

Definition 2.39 (Symmetric states). Given a group G and a unitary representation U_g , a state σ is called symmetric if and only if

$$\sigma = U_g \sigma U_g^\dagger, \quad \forall g \in G. \quad (2.46)$$

The connection with the previous discussion is that, in fact, the set of symmetric states coincides with the quantum states that can be written as a *G-twirling*:

$$\mathcal{G}(\rho) = \rho \Rightarrow \mathcal{U}_s(\rho) = \mathcal{U}_s \circ \mathcal{G}(\rho) = \int_G dg \mathcal{U}_{s \cdot g}(\rho) = \int_G dg' \mathcal{U}_{g'}(\rho) = \mathcal{G}(\rho) = \rho \quad \forall s \in G;$$

$$\mathcal{U}_g(\rho) = \rho \quad \forall g \in G \Rightarrow \rho = \int_G dg \mathcal{U}_g(\rho) = \mathcal{G}(\rho).$$

This also confirms the following expected fact: if Alice and Bob do not share a common reference frame, they can only exchange information that is invariant under the group action (i.e., information encoded in so-called “relational” degrees of freedom). To make a concrete classical example, Alice may communicate an angle to Bob by sending him two arrows, as the information is then encoded in a relational degree of freedom that is

⁸A group *representation* is a homomorphism $g \mapsto U_g$ between a group G and linear operators on a vector space $\mathcal{H}$. U_g defines the action of G on the vectors of $\mathcal{H}$.

⁹Without entering into details, if G is a finite group this expression is just an average over all group elements. If the group is a Lie group, a measure is given by the Haar measure.

invariant under global rotations. Any other directional information is lost.

Example 2.40. Let $G = SU(2)$ and $\mathcal{H}$ be $d = 2$ Hilbert space. An irreducible representation, or irrep¹⁰, is given by $\theta \mapsto U_\theta$, where U_θ parametrises the set of 2×2 special unitary matrices (here θ denotes the choice of an axis and an angle). Sometimes we denote $(\mathcal{H}, U_\theta) := \mathcal{H}_{1/2}$, and we say that “ $\mathcal{H}$ carries a spin $1/2$ irrep of $SU(2)$ ”. Among pure qubit states, none is symmetric. On the other hand, consider the two qubit space $\mathcal{H} \otimes \mathcal{H}$, where each space carries a copy of the single-qubit irrep, i.e. $\theta \mapsto U_\theta \otimes U_\theta$. This is not an irrep, but it can be decomposed as direct sum of irreps. In particular, using standard results from the theory of angular momentum, $\mathcal{H}_{1/2} \otimes \mathcal{H}_{1/2} = \mathcal{H}_0 \oplus \mathcal{H}_1$, where $\mathcal{H}_0$ carries a trivial representation (i.e. $SU(2)$ acts like the identity on $\mathcal{H}_0$). $\mathcal{H}_0$, also called singlet space, is one-dimensional and spanned by $|\psi^-\rangle = (|01\rangle - |10\rangle)/\sqrt{2}$ ($\mathcal{H}_1$ is the triplet space). $|\psi^-\rangle$ is a symmetric state.

Let us now extend this discussion to quantum operations. Assume that Bob sends to Alice a quantum state described by ρ in his reference frame. Alice then performs a quantum operation $\mathcal{E}$ on this state, relative to her reference frame. How does Bob describe the final state? If Bob knew the relation between his and her reference, he could describe this as follows: first, transform ρ into Alice’s frame, $\rho \mapsto \mathcal{U}_g^\dagger(\rho)$. Then, apply $\mathcal{E}$, and finally transform back to the original frame. Hence, with respect to Bob’s reference frame, Alice’s action would be described as $\mathcal{U}_g \circ \mathcal{E} \circ \mathcal{U}_g^\dagger(\rho)$. Since Bob has no information about g , he will describe the quantum operation as

$$\mathcal{G}(\mathcal{E}) := \int_G \mathcal{U}_g \circ \mathcal{E} \circ \mathcal{U}_g^\dagger(\rho) dg. \quad (2.47)$$

All quantum operations that can be written as a (super) G -twirling are called *symmetric* or *G -covariant*. The reason is that they coincide with the quantum operations satisfying the following

Definition 2.41 (Symmetric quantum operation). Given a group G and a unitary representation U_g , a quantum operation $\mathcal{E}$ is called symmetric (or G -covariant) if

$$\mathcal{E} = \mathcal{U}_g \circ \mathcal{E} \circ \mathcal{U}_g^\dagger, \quad \forall g \in G. \quad (2.48)$$

Example 2.42. If $\mathcal{E}$ is a unitary V and G is a connected and simply connected Lie group generated by $N_1, \dots, N_n$, the condition of Eq. (2.48) coincides with the requirement that $[V, N_i] = 0$ for $i = 1, \dots, n$. For example, for the $U(1)$ group generated by the Hamiltonian H , this simply corresponds to the condition that V conserves energy, $[V, H] = 0$.

This discussion gives the motivation to define a resource theory of asymmetry:

Definition 2.43 (Resource theory of asymmetry). Given a group G , define

1. *Free operations*: all quantum operations symmetric with respect to the action of G .

¹⁰A representation is *irreducible* in the sense that the action on the vector space does not leave invariant any non-trivial subspace of $\mathcal{H}$.

2. *Free states*: all states symmetric with respect to the action of G .

Asymmetric states, in analogy to entangled states, constitute a resource that allows transformations otherwise impossible under a symmetry constraint. As we said, reference frames are useful as they are asymmetric under a correspondent group action. More precisely, their sensitivity to the group action can be quantified by monotones under symmetric operations.¹¹ One monotone can be defined in a very similar way as before. Let $A(\rho) := S(\mathcal{G}(\rho)) - S(\rho)$ [40], called *asymmetry*. We have [44]

Lemma 2.44. $A(\rho)$ is a monotone under symmetric operations.

Proof. Using the properties of the Hilbert-Schmidt scalar product and the fact that $\mathcal{G}^2 = \mathcal{G}$, $S(\mathcal{G}(\rho)) = -\text{Tr}[\mathcal{G}(\rho) \log \mathcal{G}(\rho)] = -\text{Tr}[\rho \log \mathcal{G}(\rho)]$. From this and the definition of relative entropy it follows $A(\rho) = S(\rho || \mathcal{G}(\rho))$. Then, if $\mathcal{E}$ is covariant,

$$A(\mathcal{E}(\rho)) = S(\mathcal{E}(\rho) || \mathcal{G}(\mathcal{E}(\rho))) = S(\mathcal{E}(\rho) || \mathcal{E}(\mathcal{G}(\rho))) \leq S(\rho || \mathcal{G}(\rho)) = A(\rho), \quad (2.49)$$

where we used the contractivity of the relative entropy under quantum channels. ■

Beyond Noether's theorem with asymmetry [45]

Why should we care about the resource theory of asymmetry? Symmetry constraints for closed system dynamics of *pure* quantum states are encoded by the conservation of all moments of the generators of the symmetry group. However, this is not the case for mixed quantum states and/or open quantum system dynamics. Asymmetry monotones can impose further, non-trivial constraints on the dynamics.

Consider a system described by $\mathcal{H} \otimes \mathcal{H}_a$ where $\mathcal{H}$ is a qubit system and $\mathcal{H}_a$ is an ancilla. Then define the two states

$$\rho = \frac{1}{2} |0\rangle\langle 0| \otimes |s_1\rangle\langle s_1| + \frac{1}{2} |1\rangle\langle 1| \otimes |s_2\rangle\langle s_2|, \quad \xi = \frac{1}{2} |+\rangle\langle +| \otimes |s_1\rangle\langle s_1| + \frac{1}{2} |-\rangle\langle -| \otimes |s_2\rangle\langle s_2|,$$

where $|0\rangle, |1\rangle$ are eigenstates of the Pauli Z operator and $|\pm\rangle$ are eigenstates of the Pauli X operator. Assume now that we can only perform rotationally symmetric dynamics and that $|s_1\rangle, |s_2\rangle$ are two orthogonal states, symmetric under rotations (e.g. the eigenstates of a rotationally invariant observable). Is it possible that the dynamics transforms ρ into σ ? The generators of the symmetry are $\sigma_i \otimes L_j$, where $\sigma_1 = X, \sigma_2 = Y, \sigma_3 = Z$ and L_j are angular momentum operators on $\mathcal{H}_a$. Because the states $|s_i\rangle$ are symmetric, and the reduced state on the first system is maximally mixed, one finds, for both ρ and ξ , $\text{Tr}[\rho \sigma_i \otimes L_j] = \text{Tr}[\xi \sigma_i \otimes L_j]$ for all i, j . So all generators of the symmetry are conserved quantities. Nevertheless, there is no symmetric transformation mapping ρ into σ . This is easily captured by monotones: one can show that $\log 2 = A(\xi) > A(\rho) = 0$. To see this, note that

$$\mathcal{G}(\xi) = \frac{\mathbb{I}}{4} \otimes |s_1\rangle\langle s_1| + \frac{\mathbb{I}}{4} \otimes |s_2\rangle\langle s_2|. \quad (2.50)$$

Hence, $A(\xi) = S([1/2, 0, 0, 1/2] || [1/4, 1/4, 1/4, 1/4]) = \log 2$.

¹¹This is intuitive: the property of breaking a symmetry cannot be increased by symmetric operations.

3 Stochastic independence as a resource in small-scale thermodynamics

3.1 Introduction

In the first part of this thesis we will focus on the role of correlations in non-equilibrium thermodynamics. We consider the general scenario introduced in Section 2.2.2 where, given a system in any out-of-equilibrium state ρ , we want to obtain a target state σ by means of a Thermal Operation. Moreover, we will allow for the use of auxiliary systems $c_1, \dots, c_N$ that catalyze the transformation but are given back unchanged (an idea introduced in Section 2.1.5). Severe constraints need to be met for such a transformation to exist, essentially the free energy second laws of Theorem 2.26. We study here what happens if we allow the auxiliary systems to get correlated in the process (see Fig. 3.1).

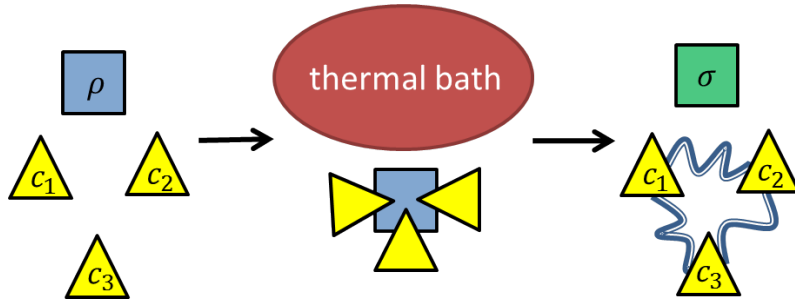


Figure 3.1. The general scenario: a quantum state ρ , with eigenvalues x , is transformed into a state σ , with eigenvalues y , exploiting a thermal bath at temperature T_B and auxiliary systems that ease the transformation, but are given back unchanged at the end. If correlations can be created among the auxiliary systems and the states involved are incoherent, we prove that such a transformation is possible if and only if $F(x) \geq F(y)$.

At first glance, it seems that this cannot be of any help, because the creation of correlations increases the free energy of the auxiliary systems. Hence, the argument goes, the creation of correlations is yet another obstacle to the requirement that the free energy has to decrease in the process. However, as we have seen in the previous chapter, there is much more to single-shot thermodynamics than just “the” free energy. Surprisingly, we show that the creation of correlations greatly enlarges the set of states that can be obtained from ρ . Indeed, any transformation that decreases the regular free energy $F(x) = \sum_i x_i E_i - kT_B H(x)$ becomes possible in the single-shot regime, when no coherence is present (the role of coherence is discussed in the next chapters). As we will make

clear, all transformations that would be possible in the “thermodynamic limit” of processing $n \rightarrow \infty$ uncorrelated copies of a system become possible on individual systems. This gives a single-shot operational meaning to the regular free energy and shows that if an engine can access uncorrelated auxiliary systems, it can operate as if it was reversible, even in extreme thermodynamic regimes. We also show that the correlations that one needs to create for this purpose are always vanishingly small.

3.1.1 Severe limitations of small-scale thermodynamics

As mentioned in the introduction, given a state ρ we assume we are allowed to perform any Thermal Operation on it. We also allow for the use of catalysts, i.e., auxiliary systems that facilitate the transformation, but are given back at the end unchanged and uncorrelated from all other systems. These transformations are called *catalytic Thermal Operations*:

Definition 3.1 (Catalytic Thermal Operations [23]). We say that there exists a *catalytic Thermal Operation* mapping ρ to σ , and write $\rho \xrightarrow{cto} \sigma$, if there is a catalyst c and a Thermal Operation $\mathcal{T}$ such that $\mathcal{T}(\rho \otimes c) = \sigma \otimes c$.

When the states are incoherent, Proposition 2.36 allows us to reduce the problem of finding a Thermal Operation to a question about the eigenvalues of the initial and final states. We will need the following definition:

Definition 3.2. Consider a system with Hamiltonian H . Let Π_i be the projectors on the eigenspaces of H . The dephasing operator D_H is defined as

$$D_H(\cdot) = \sum_i \Pi_i(\cdot)\Pi_i. \quad (3.1)$$

Recall the definition of the family of generalized free energies, $\{F_\alpha\}$, introduced in Section 2.1.5. We have

Theorem 3.3. [23] Let ρ, σ be quantum states block-diagonal in the energy eigenbasis, with eigenvalues $\mathbf{x}$ and $\mathbf{y}$. Let σ_ϵ be a sequence of incoherent states, with $\sigma_\epsilon \rightarrow \sigma$ as $\epsilon \rightarrow 0$. Then $\rho \xrightarrow{cto} \sigma_\epsilon$ for all $\epsilon \geq 0$ if and only if

$$F_\alpha(\mathbf{x}) \geq F_\alpha(\mathbf{y}), \quad \forall \alpha \in \mathbb{R}. \quad (3.2)$$

The catalyst can always be chosen to have trivial Hamiltonian.

Proof. Let σ_ϵ be a sequence as above, and $\mathcal{T}_\epsilon, c_\epsilon$ Thermal Operations and catalysts satisfying $\mathcal{T}_\epsilon(\rho \otimes c_\epsilon) = \sigma_\epsilon \otimes c_\epsilon, \forall \epsilon \geq 0$. One can check that $\mathcal{T}_\epsilon$ commutes with the dephasing operator $D_{H_{SC}}$, where $H_{SC} = H_S + H_C$, with H_S the Hamiltonian of the system and H_C the Hamiltonian of the catalyst. Then,

$$\mathcal{T}_\epsilon(\rho \otimes D_{H_C}(c_\epsilon)) = \sigma_\epsilon \otimes D_{H_C}(c_\epsilon). \quad (3.3)$$

This shows that the catalyst can always be chosen to be incoherent. Hence $\rho \xrightarrow{cto} \sigma_\epsilon$ is a transformation involving only incoherent states. Theorem 2.38 then allows us to equivalently rewrite the claim as follows: for any $\epsilon > 0$ there exists $\mathbf{a}_\epsilon$ and $\mathbf{y}_\epsilon$, with $\|\mathbf{y}_\epsilon - \mathbf{y}\| \leq \epsilon$, such that

$$\mathbf{x} \otimes \mathbf{a}_\epsilon \succ_g \mathbf{y}_\epsilon \otimes \mathbf{a}_\epsilon, \quad (3.4)$$

if and only if Eq. (3.2) holds. However this is content of Theorem 2.26. From the proof of such theorem, the Hamiltonian of the catalysts can be chosen to be trivial. ■

Deterministic transformations between non-equilibrium states are severely limited by these constraints. If we look at the asymptotic (or “thermodynamic”) limit in which we process simultaneously a large number $n \rightarrow \infty$ of independent and identically distributed (i.i.d.) states, then all these conditions reduce to the single condition that the free energy F has to decrease. This is captured by the following theorem [33]:¹

Theorem 3.4. *Let ρ and σ be two incoherent quantum states. Let R be the largest number such that for every $\epsilon > 0$ there exists $\bar{n} \in \mathbb{N}$ and a Thermal Operation $\mathcal{T}$ with*

$$\|\mathcal{T}(\rho^{\otimes \bar{n}}) - \sigma^{\otimes R\bar{n}}\| \leq \epsilon. \quad (3.5)$$

One has $R = \Delta F(\rho) / \Delta F(\sigma)$, where (see Eq. (2.42))

$$\Delta F(\rho) = F(\rho) - F(\gamma_S), \quad F(\rho) = \text{Tr}[H_S \rho] - kT_B S(\rho). \quad (3.6)$$

Note that $F(\rho) = F(\mathbf{x})$, where $\mathbf{x}$ are the eigenvalues of ρ , because ρ is block-diagonal. F also coincides with the thermodynamic free energy when computed on equilibrium states: as $\gamma_S = e^{-\beta H_S} / Z_{H_S}$, $F(\gamma_S) = -kT_B \log Z_{H_S}$. However, non-equilibrium thermodynamics of few systems (or many, but correlated) is governed by all $\{F_\alpha\}$. Far from equilibrium processes and non-negligible correlations are expected to be common at small scales, so the $\{F_\alpha\}$ may be relevant in this regime.

Remark 3.5 (Open question). It would be useful to know how large $\bar{n}$ must be to give a good approximation of the target state. In other words, how quickly thermodynamically interesting transformations such as work extraction converge to the rate given by the previous theorem.

3.1.2 A paradigmatic example of the role of correlations

To better understand the issues at hand, before presenting our general result we consider a paradigmatic example. Suppose we are given a qubit system, with Hamiltonian $H_S = E|1\rangle\langle 1|$ and in an incoherent state with population p in the ground state. To extract work from it, we are allowed to perform any catalytic Thermal Operation (for a brief review of work extraction within the resource theory approach, see box below)

¹In the cited paper the theorem is given in full generality for arbitrary quantum states. However, there are subtleties concerning the use of a coherence source.

Work extraction: a brief summary

In thermodynamics we are often interested in transforming thermal energy into usable work. Here we briefly discuss aspects of work extraction and clarify some connections with standard treatments. Assume we are given a qubit system, initially in the state $|0\rangle$ and degenerate in energy. How much work can be extracted if we have at our disposal a thermal bath at temperature T_B ? This is basically the inverse process of Landauer erasure and would give us an amount of work $w = kT_B \log 2$ (see [37] for a review). A standard way to see this is to begin changing the Hamiltonian of the system (with the bath disconnected), in such a way that $|0\rangle$ is thermal with respect to the new Hamiltonian. This is achieved by raising the unoccupied energy level $|1\rangle$ very high (formally, to infinity) and can be done at no work cost as this level has no population. One then puts the system in contact with the bath and quasi-statically lowers the level down (this can be understood as a limiting process of small energy level changes intertwined by thermalisations). At the final time, the Hamiltonian is again degenerate, the final state is maximally mixed and we extracted $w = \int_{+\infty}^0 e^{-\beta E} / (1 + e^{-\beta E}) dE = kT_B \log 2$.

The resource theory framework gives a more satisfactory picture, in which work is stored in an explicit system rather than in the classical external field. Consider a battery system initially in the ground state $|0\rangle_{\text{bat}}$. We look for a (catalytic) Thermal Operation exciting the battery while leaving the final state of the system maximally mixed:

$$|0\rangle\langle 0| \otimes |0\rangle\langle 0|_{\text{bat}} \xrightarrow{\text{cto}} \frac{\mathbb{I}}{2} \otimes |w\rangle\langle w|_{\text{bat}}. \quad (3.7)$$

As the initial and final Hamiltonians are degenerate (and all states are incoherent), the constraints of Theorem 3.3 give $w = kT_B \log 2$. This coincides with the standard protocol. Things become more complicated when the initial state is mixed, with population given by some initial probability distribution $\mathbf{p}$. The first step of the standard protocol will, in fact, cost a fluctuating amount of work. Standard techniques then focus on computing the average work yield, which is seen to be equal to $\langle w \rangle = kT_B (\log d - H(\mathbf{p}))$, if d is the dimension of the system [46]. Even more generally, for a system described by an initial Hamiltonian H_S , $\langle w \rangle = F(\mathbf{p}) - F(\mathbf{g}) = kT_B \log Z_{H_S} + \langle H_S \rangle - kT_B H(\mathbf{p})$. This can be obtained following a similar protocol as before. If $H_S = E_i |1\rangle\langle 1|$, move $|1\rangle$ from E_i to E_f such that $p = 1/(1 + e^{-\beta E_f})$ and the state is thermal with respect to the new Hamiltonian. The cost of this step is, *on average*, $c = (E_f - E_i)(1 - p)$, with $E_f = kT_B \log p - kT_B \log(1 - p)$. We then quasi-statically bring back E_f to E_i , while keeping the system in contact to the bath, extracting $t = \int_{E_1}^{E_0} e^{-\beta E} / (1 + e^{-\beta E}) = kT_B \log p + kT \log(1 + e^{-\beta E})$. One then finds $\langle w \rangle = t - c$ has the expression given, a difference of free energies.

However, fluctuations can be large [46]. The resource theory, on the other hand, gives results about deterministic work extraction. From Theorem 3.4, we obtain deterministic work $w = kT_B (\log d - H(\mathbf{p}))$ only in the asymptotic limit, otherwise the maximum deterministic work is computed to be $w = kT_B (\log d - H_0(\mathbf{p})) \leq \langle w \rangle$. One generally gets substantially less work if we require it to be fluctuation-free; the reason why the two approaches coincide in the asymptotic limit is that fluctuations die out, so that the average can be achieved deterministically. But for a small number of systems, when fluctuations cannot be neglected, resource theories give a new way of posing questions beyond averages that are not usually considered in standard approaches.

Following [23, 24], work extraction is explicitly modelled by introducing a “work bit”, i.e. a two-level system with Hamiltonian $H_W = w |1\rangle\langle 1|$ that is initially in the ground state $|0\rangle$ and at the end of the transformation is found with high probability in the excited state $|1\rangle$.² If $\gamma_S = e^{-\beta H_S} / Z_{H_S}$ work extraction can be modelled as the transformation of Fig. 3.2:

$$\rho \otimes |0\rangle\langle 0| \xrightarrow{cto} \gamma_S \otimes \chi_\epsilon(w), \quad (3.8)$$

$$\chi_\epsilon(w) = \epsilon |0\rangle\langle 0| + (1 - \epsilon) |1\rangle\langle 1|. \quad (3.9)$$

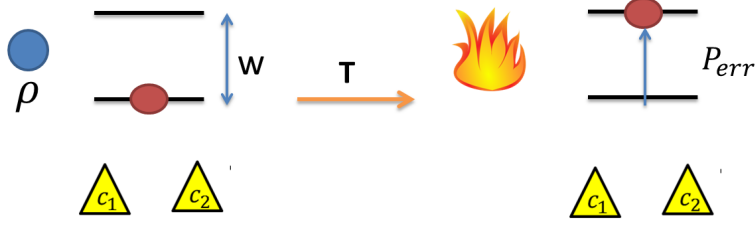


Figure 3.2. A paradigmatic example: an incoherent out-of-equilibrium state, initially described by ρ , is thermalised, while a work bit is excited (with error probability $p_{err} = \epsilon$). Any number of catalysts can aid the transition. For a particular choice of parameters, this transformation is provably impossible for any choice of the catalysts. However, we show that if correlations are created among two auxiliary systems, then the transformation becomes thermodynamically possible.

Consider for example the choices $\beta E = 1$, $\beta w = 0.01$, $p = 0.73$, $\epsilon = 0.007$ in Eq. (3.8). The free energy $F_1 \equiv F$ decreases, $\Delta F < 0$. However for other F_α this is not the case. One can compute, from Eq. (3.8),

$$\frac{\Delta F_\alpha}{kT_B} = -\log(1 + e^{-\beta E}) + \frac{1}{\alpha - 1} \log \frac{\epsilon^\alpha + (1 - \epsilon)^\alpha e^{-\beta w(1 - \alpha)}}{p^\alpha + (1 - p)^\alpha e^{-\beta E(1 - \alpha)}} \quad (3.10)$$

and check that there is a range of α 's for which $\Delta F_\alpha > 0$, see Fig. 3.3 (e.g., take $\alpha = 4$).

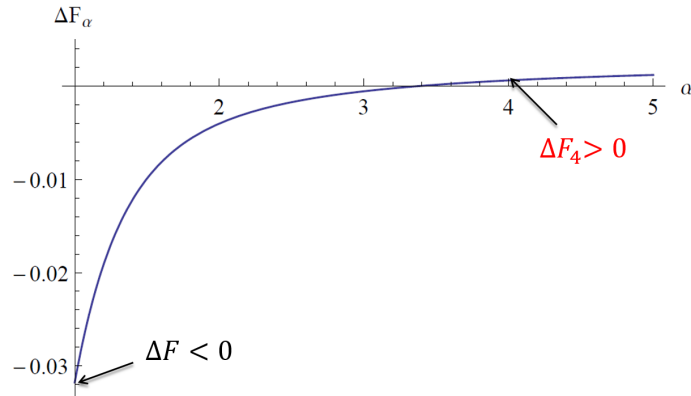


Figure 3.3. The many constraints of small scale thermodynamics: change in the family of free energies F_α in the transformation of Eq. (3.8), for the choices of parameters given in the text. Even if $F_1(x) \equiv F(x) = U(x) - kT_B H(x)$ is decreasing, the transformation is impossible because some of the generalised free energies increase.

²This may be a resonant transition of a larger system.

Hence, due to Theorem 3.3, no catalytic Thermal Operation can perform the work extraction of Eq. (3.8), despite $\Delta F < 0$. We stress that this means that no matter what catalysts we use or how many, the work extraction transition introduced above is impossible.

Reconsider however the transformation in Eq. (3.8), and now let us use two auxiliary systems c_1, c_2 that can get correlated in the process, without changing their local states. These are taken to have trivial Hamiltonian and ground state occupations equal to s and q , respectively. We ask now if there exists $\mathcal{T}$ satisfying

$$\mathcal{T}(\rho \otimes |0\rangle\langle 0| \otimes c_1 \otimes c_2) \stackrel{?}{=} \gamma_S \otimes \chi_\epsilon(w) \otimes c_{12}, \quad (3.11)$$

where c_{12} has marginals c_1 and c_2 . Here c_{12} is the final, correlated state of the two auxiliary systems. Choose $s = 0.95$, $q = 0.70$, and let c_{12} have eigenvalues

$$(x_{00}, x_{01}, x_{10}, x_{11}) = (0.66, 0.29, 0.04, 0.01). \quad (3.12)$$

The process created correlations between the auxiliary systems without changing their marginals, as in Fig. 3.1. One can check that, despite the correlations, we still have $\Delta F < 0$. Constructing the thermo-majorisation curve for this process one can show that the eigenvalues of the initial state in Eq. (3.11) thermo-majorise those of the right-hand-side. Hence, from Theorem 2.38, a Thermal Operation $\mathcal{T}$ exists inducing this transition.

This may seem puzzling: if the process in Eq. (3.8) is impossible, why is (3.11) now possible? To understand this, we need to reconsider the notion of entropy for non-equilibrium systems.

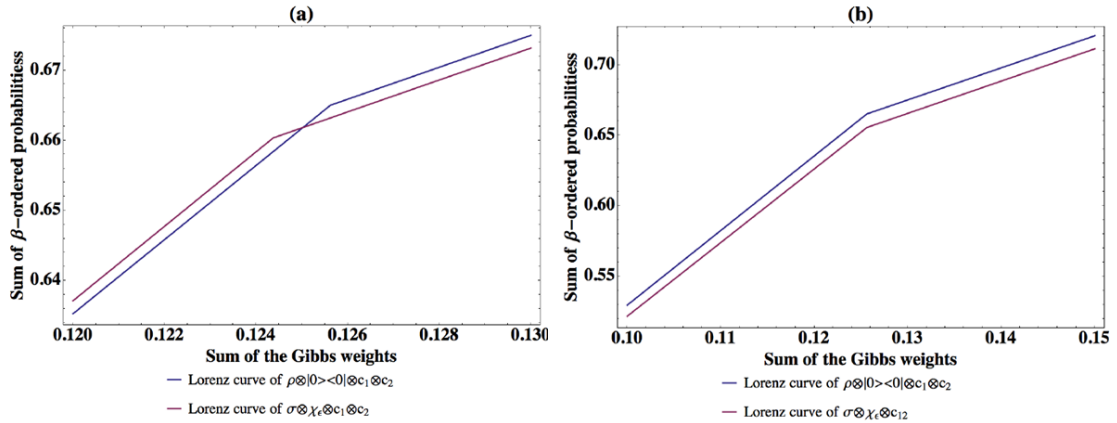


Figure 3.4. The power of correlations: detail of the (rescaled) thermomajorisation curves of the initial (red) and final (blue) state for the transition of Eq. (3.11). In (a) no correlations are created (i.e. $c_{12} = c_1 \otimes c_2$). In (b), correlations are created without changing the marginal, according to Eq. (3.12). We see that whereas in (a) the curves intersect, in (b) they do not. From the theory reviewed in Chapter 2, and the results presented in Fig. 3.3, this means that the creation of correlations is what makes the transformation (3.11) possible.

3.2 The role of correlations in small scale thermodynamics

3.2.1 Anomalous α -entropy production

Non-equilibrium thermodynamics of small systems presents severe challenges, but we can turn some peculiar features of this regime to our advantage. One striking difference between non-equilibrium and equilibrium thermodynamics is that in the latter a unique entropy function exists, characterizing the thermodynamics of the systems at hand, whereas out of equilibrium this will not be the case (see Chapter 2). Therefore, the existence of a family of free energies $\{F_\alpha\}$ is not a mathematical curiosity with no bearing on physics, but is tightly linked to the fundamental properties of non-equilibrium systems. This gives the multiple constraints of Theorem 3.3 but also – as we shall now see – a key and counterintuitive property of correlations: they can generate entropy while being created.

Theorem 3.3 shows that the catalysts used in the thermodynamic processes can always be chosen to have trivial Hamiltonians. Hence, the free energies of the catalysts are given by $F_\alpha = -kT_B H_\alpha$.

Because we usually deal with “the” entropy $H(\cdot)$, we have some hard-wired intuitions about the connection between correlations and entropy. For example, we expect two uncorrelated probability distributions to become “less disordered” when correlations are created (without changing the marginals). Intuitively this is because knowing the realization of one of them allows (due to correlations) to more easily guess the realization of the other. This is captured by the well-known subadditivity of entropy and by the relation

$$H(\mathbf{p}_{AB}) = H(\mathbf{p}_A) + H(\mathbf{p}_B) - I(\mathbf{p}_{AB}), \quad (3.13)$$

where $I(\mathbf{p}_{AB})$ (implicitly defined by Eq. (3.13)) is the mutual information between A and B , and $\mathbf{p}_A, \mathbf{p}_B$ are the marginals of the joint distribution $\mathbf{p}_{AB}$. One has $I(\mathbf{p}_{AB}) \geq 0$ (and $I(\mathbf{p}_{AB}) = 0$ if and only if $\mathbf{p}_{AB} = \mathbf{p}_A \otimes \mathbf{p}_B$), since $H(\mathbf{p}_{AB}) < H(\mathbf{p}_A \otimes \mathbf{p}_B)$ whenever $\mathbf{p}_{AB}$ is correlated. It seems that creating correlations has an average work cost [47–50], because it leads to a reduction of entropy.

However, as discussed above, for non-equilibrium processes we are forced to use many notions of entropy and some of them are at odds with this intuition. In other words, the creation of correlations can be associated to an entropy *production*:

$$H_\alpha(\mathbf{p}_A \otimes \mathbf{p}_B) < H_\alpha(\mathbf{p}_{AB}). \quad (3.14)$$

We call this property “anomalous α -entropy production”. If, for some $\alpha \neq 1$, Eq. (3.14) holds for some distribution $\mathbf{p}_{AB}$, then the creation of correlations may ease the thermodynamic transformations. Indeed, we will see that the creation of correlations between the auxiliary systems used in the process massively enlarges the set of accessible states and allows one to extract much more high-quality work than would have been possible

otherwise. The non-uniqueness of entropy carries physical consequences at odds with what is expected in the regimes where one entropy provides a complete description. The following result shows that what we came across in the example of the previous section is a general thermodynamical property.

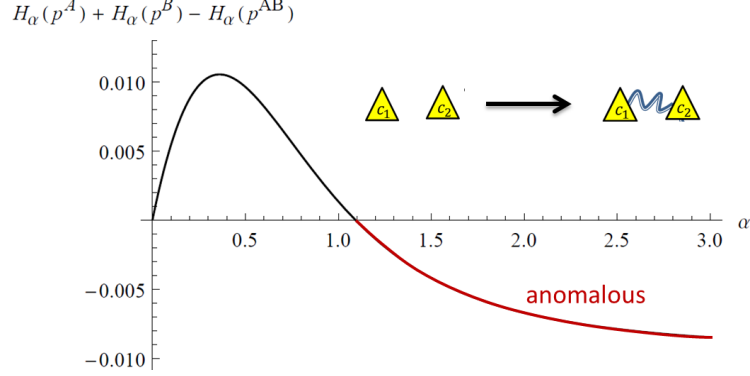


Figure 3.5. Anomalous entropy production: α -entropy production, in the auxiliary systems due to the creation of correlations in the transformation of Eq. (3.11), with the choice of Eq. (3.12). There is an anomalous entropy production for every α from about $\alpha = 1.1$ up to $\alpha = +\infty$.

3.2.2 A general thermodynamic property

Let us denote by $c_1, \dots, c_N$ the marginals of an N -partite system $c_{1,\dots,N}$. The general thermodynamical property is the following: whenever we are given two states that satisfy $\Delta F \leq 0$, we can find auxiliary systems and correlations among them that make the transformation thermodynamically possible. The notation $\text{Tr}_{\setminus i}[\cdot]$ indicates the trace over all system excluding i . Then,

Theorem 3.6. *Consider a system with Hamiltonian H_S and states ρ and σ block-diagonal in energy, with $\mathbf{p}$ and $\mathbf{q}$ the respective eigenvalues. The three following statements are equivalent:*

1. *There exists a Thermal Operation $\mathcal{T}$ transforming ρ into a state σ_ϵ arbitrarily close to σ , by creating correlations among incoherent auxiliary systems, but without changing their local states:*

$$\mathcal{T}(\rho \otimes c_1 \otimes \dots \otimes c_N) = \sigma_\epsilon \otimes c_{1,\dots,N}. \quad (3.15)$$

with $\text{Tr}_{\setminus i}[c_{1,\dots,N}] = c_i$ for $i = 1, \dots, N$. One can always choose $N \leq 3$ and trivial Hamiltonians for the auxiliary systems.

2. *There exists incoherent states $c_1, \dots, c_N$ and $c_{1,\dots,N}$ s.t. the anomalous α -entropy production ensures that all $\{F_\alpha\}$ constraints of Theorem 3.3 are satisfied.*
3. *$F(\mathbf{p}) \geq F(\mathbf{q})$.*

The proof is based on a generalization of the notion of catalytic majorization introduced in [51] and is reported in the next subsection.

3.2.3 Proof of Theorem 3.6

The structure of the proof is as follows. First, we recall a recent result on the theory of majorization [51] and show that it immediately implies the general result of Theorem 3.6 in the special case in which the Hamiltonians of all systems involved are trivial. We then use techniques introduced in Section 2.1.4 to extend the result to thermodynamics with general Hamiltonians. In this work we assume that all systems are finite-dimensional.

Result for trivial Hamiltonians

The first step is to recall a recent characterization of von Neumann entropy through a generalized notion of majorization, introduced in [51]. While the results there have originally been formulated for classical probability distributions, it is easy to see that they carry over directly to quantum states, by identifying the vector of eigenvalues with a probability distribution:

Definition 3.7 (Majorisation for quantum states). Let ρ and σ be general quantum states, with eigenvalues $\mathbf{p}$ and $\mathbf{q}$, respectively. We say $\rho \succ \sigma$ if and only if $\mathbf{p} \succ \mathbf{q}$.

Definition 3.8 (c-trumping, [51]). We say that ρ *c-trumps* σ , and write $\rho \succ^c \sigma$, if and only if there exists $N \in \mathbb{N}_0$ and a N -partite quantum state $c_{1,2,\dots,N}$, with marginals $c_1, \dots, c_N$, such that

$$\rho \otimes (c_1 \otimes \dots \otimes c_N) \succ \sigma \otimes c_{1,2,\dots,N}. \quad (3.16)$$

Notice that majorization is a special case of c-trumping when $N = 0$ and trumping (Def. 2.19) is a special case when $N = 1$. We can now report one main result of [51]:

Theorem 3.9. Suppose that ρ and σ do not have identical sets of eigenvalues. Then $\rho \succ^c \sigma$ if and only if $\text{rank}(\rho) \leq \text{rank}(\sigma)$ and $S(\rho) < S(\sigma)$. Moreover, we can always choose $N = 3$ in (3.16).

Here $S(\rho)$ is the von Neumann entropy of ρ . We can now show that this result immediately implies a result valid for thermodynamics, when the Hamiltonians of all systems are trivial. We denote by $\|\cdot\|$ the trace norm $\|X\| = \text{Tr} [\sqrt{X^\dagger X}]$. However note that the following result actually holds for any general norm, as all norms are equivalent in finite dimension.

Lemma 3.10. Consider a system with trivial Hamiltonian. The following statements are equivalent:

1. For every $\epsilon > 0$ there exists a Thermal Operation $\mathcal{T}_\epsilon$ involving a bath in a maximally mixed state and N auxiliary systems with trivial Hamiltonians, joint state $c_{1,\dots,N}$ and marginals $c_1, \dots, c_N$ such that

- a) $\|\sigma - \sigma_\epsilon\| < \epsilon$,
- b) $\mathcal{T}_\epsilon(\rho \otimes c_1 \otimes \dots \otimes c_N) = \sigma_\epsilon \otimes c_{1,\dots,N}$.

One can always choose $N \leq 3$.

2. $S(\rho) \leq S(\sigma)$.

Mathematical Aside 3.1. Proof of Lemma 3.10

When Hamiltonians are trivial, Thermal Operations take the form

$$\mathcal{T}(\rho) = \text{Tr}_2 [U(\rho \otimes \eta)U^\dagger], \quad (3.17)$$

where η is a maximally mixed state of any dimension and U is an arbitrary unitary. However, this is the definition of a noisy operation [52, 53]. Furthermore, the existence of a noisy operation (mapping a given initial state arbitrarily close to a given target state) is equivalent to the majorization condition [52], so we conclude that $1 \Leftrightarrow 1'$, where

1'. For every $\epsilon > 0$

a) $\|\sigma - \sigma_\epsilon\| < \epsilon,$

b) $\rho \otimes c_1 \otimes \cdots \otimes c_N \succ \sigma_\epsilon \otimes c_{1,\dots,N}.$

Then $1' \Rightarrow 2$. Schur-concavity and subadditivity of S imply $S(\rho) \leq S(\sigma_\epsilon)$ for every $\epsilon > 0$. In fact,

$$S(\rho) \leq S(\sigma_\epsilon) + [S(c_{1,\dots,N}) - S(c_1 \otimes \cdots \otimes c_n)] \leq S(\sigma_\epsilon). \quad (3.18)$$

Then, by continuity, taking $\epsilon \rightarrow 0$ gives $S(\rho) \leq S(\sigma)$.

Conversely, given $S(\rho) \leq S(\sigma)$, for any $0 < \delta < 1$ we can define the state $\sigma_\delta := (1 - \delta)\sigma + \delta\mathbb{I}/d$, where d is here the dimension of the Hilbert space of the system that carries the state ρ . Clearly, for any fixed ϵ , there exists δ small enough such that $\|\sigma - \sigma_\delta\| \leq \epsilon$. Since S is strictly concave, we get $S(\rho) \leq S(\sigma) < S(\sigma_\delta)$. Also, by construction, $\text{rank}(\rho) \leq \text{rank}(\sigma_\delta)$. Hence, Theorem 3.9 implies $1'$. This concludes the proof that $1' \Leftrightarrow 2$ and hence $1 \Leftrightarrow 2$.

Result for non-trivial Hamiltonians

We can now use the embedding map to generalise this result to non-trivial Hamiltonians. Recall that the embedding maps probability distributions from $\mathbb{R}^n$ in $\mathbb{R}^D$ via $\mathbf{p} \mapsto \Gamma_{\mathbf{d}}(\mathbf{p})$ (see Def. 2.12). If ρ is a quantum state block-diagonal in energy – with occupations given by $\mathbf{p}$ and corresponding Gibbs distribution $\mathbf{g}$ – then the free energies of $\mathbf{p}$ can be computed from the entropies of the embedded distribution. In fact, from Eq. (2.34),

$$F_\alpha(\mathbf{p}) - F_\alpha(\mathbf{g}) = kT_B \left(\text{sgn}(\alpha) \log D - H_\alpha(\Gamma_{\mathbf{d}}(\mathbf{p})) \right). \quad (3.19)$$

We now rewrite Theorem 3.6 in order to make all the claims mathematically precise. As before, $\|\cdot\|$ can be any norm. Let $\mathbf{p}, \mathbf{q}, \mathbf{q}_\epsilon, \mathbf{c}_i, \mathbf{c}_{1,\dots,N}$ be the vectors of the respective eigenvalues of $\rho, \sigma, \sigma_\epsilon, c_i, c_{1,\dots,N}$. Then,

Theorem 3.11. *Consider a system with Hamiltonian H_S and states ρ and σ block-diagonal in energy. The three following statements are equivalent:*

1. For every $\epsilon > 0$ there exist N incoherent auxiliary systems with some Hamiltonians, in a state $c_{1,\dots,N}$ with marginals $c_1, \dots, c_N$, and a Thermal Operation $\mathcal{T}_\epsilon$ such that

$$a) \quad \|\sigma - \sigma_\epsilon\| < \epsilon,$$

$$b) \quad \mathcal{T}_\epsilon(\rho \otimes c_1 \otimes \dots \otimes c_N) = \sigma_\epsilon \otimes c_{1,\dots,N}.$$

2. For every $\epsilon > 0$ there exists a block-diagonal state $c_{1,\dots,N}$ on N auxiliary systems with trivial Hamiltonians such that, for every $\alpha \in \mathbb{R}$,

$$F_\alpha(\mathbf{p}) - kT_B \sum_i H_\alpha(\mathbf{c}_i) \geq F_\alpha(\mathbf{q}_\epsilon) - kT_B H_\alpha(\mathbf{c}_{1,\dots,N}).$$

3. $F(\mathbf{p}) \geq F(\mathbf{q})$

Notice that $c_{1,\dots,N}$ will in general depend on ϵ . It will follow from the proof that one can always choose $N = 3$ and trivial Hamiltonians for the auxiliary systems in 1.

Proof. For the sake of the proof, we introduce two further statements that will turn out to be equivalent:

4. Identical to statement 1, but with the additional requirement that the auxiliary systems have trivial Hamiltonians.

5. For every $\epsilon > 0$ there exist N auxiliary systems with some Hamiltonians and a state $c_{1,\dots,N}$ on them such that for every $\alpha \in \mathbb{R}$,

$$F_\alpha(\mathbf{p}) + \sum_i F_\alpha(\mathbf{c}_i) \geq F_\alpha(\mathbf{q}_\epsilon) + F_\alpha(\mathbf{c}_{1,\dots,N}). \quad (3.20)$$

Clearly the implications $4 \Rightarrow 1$ and $2 \Rightarrow 5$ are trivially true.

$1 \Rightarrow 5$: Applying dephasing on both sides of the transformation shows that σ_ϵ can be chosen to be incoherent. Then, from Theorem 2.38, $\mathbf{p} \otimes \mathbf{c}_1 \otimes \dots \otimes \mathbf{c}_N \succ_g \mathbf{q}_\epsilon \otimes \mathbf{c}_{1,\dots,N}$. From the additivity of the α -free energies F_α on tensor products and g -Schur-convexity, 5 follows. The same argument proves $4 \Rightarrow 2$.

$5 \Rightarrow 3$: Take $\alpha = 1$ in Eq. (3.20). Since the total Hamiltonian on the N auxiliary systems is by definition the sum of the local Hamiltonians H_i , and due to the subadditivity of the Shannon entropy, we obtain

$$F(\mathbf{c}_{1,\dots,N}) = \sum_{i=1}^N \text{Tr} [c_i H_i] - kT_B H(\mathbf{c}_{1,\dots,N}) \geq \sum_{i=1}^N \text{Tr} [c_i H_i] - kT_B \sum_{i=1}^N H(\mathbf{c}_i) = \sum_{i=1}^N F(\mathbf{c}_i).$$

Thus, Eq. (3.20) implies $F(\mathbf{p}) \geq F(\mathbf{q}_\epsilon)$. Since this is true for all $\epsilon > 0$, and F is continuous, we also obtain $F(\mathbf{p}) \geq F(\mathbf{q})$ by taking the limit $\epsilon \rightarrow 0$.

3 $\Rightarrow$ 4: the proof is based on the techniques developed in [23] and reviewed in Sec. 2.1.4. We may assume $\mathbf{q} \neq \mathbf{g}$, otherwise 4 follows trivially, with $N = 0$ and $\mathcal{T}_\epsilon$ the map that prepares the free Gibbs state.

We consider the case that all components of γ_S are rational numbers (the generalisation to irrational numbers is a technicality and can be found in [3]). By assumption there exists then $\mathbf{d} = \{d_1, \dots, d_n\}$ such that

$$\mathbf{g} = \left\{ \frac{d_1}{D}, \frac{d_2}{D}, \dots, \frac{d_n}{D} \right\}, \quad \sum_{i=1}^n d_i = D.$$

By definition, $\Gamma_{\mathbf{d}}(\mathbf{g}) = \boldsymbol{\eta}_D$, where $\boldsymbol{\eta}_D$ is a D -dimensional uniform distribution. We can introduce an auxiliary probability distribution $\mathbf{q}_\delta = (1 - \delta) \mathbf{q} + \delta \mathbf{g}$, with $0 < \delta < 1$ such that $\|\mathbf{q} - \mathbf{q}_\delta\| \leq \epsilon$. Since Shannon entropy is strictly concave, F is strictly convex. Because $F(\mathbf{q}) < F(\mathbf{g})$,

$$F(\mathbf{q}_\delta) = F((1 - \delta) \mathbf{q} + \delta \mathbf{g}) < F(\mathbf{q}).$$

This implies

$$F(\mathbf{p}) \geq F(\mathbf{q}) > F(\mathbf{q}_\delta). \quad (3.21)$$

From Eq. (3.19), it follows that $H(\Gamma_{\mathbf{d}}(\mathbf{p})) < H(\Gamma_{\mathbf{d}}(\mathbf{q}_\delta))$. Furthermore $\text{rank}(\mathbf{p}) \leq \text{rank}(\mathbf{q}_\delta)$ by construction, and this implies $\text{rank}(\Gamma_{\mathbf{d}}(\mathbf{p})) \leq \text{rank}(\Gamma_{\mathbf{d}}(\mathbf{q}_\delta))$. Using Theorem 3.9 and the characterisation of majorisation of Theorem 2.6, this is equivalent to the existence of an auxiliary system $\mathbf{c}_{1,\dots,N}$ with marginals $\mathbf{c}_1, \dots, \mathbf{c}_N$ and a bistochastic map Λ such that

$$\begin{aligned} \Lambda(\Gamma_{\mathbf{d}}(\mathbf{p}) \otimes \mathbf{c}_1 \otimes \dots \otimes \mathbf{c}_N) &= \Gamma_{\mathbf{d}}(\mathbf{q}_\delta) \otimes \mathbf{c}_{1,\dots,N}, \\ \Lambda(\boldsymbol{\eta} \otimes \boldsymbol{\eta}_1 \otimes \dots \otimes \boldsymbol{\eta}_N) &= \boldsymbol{\eta} \otimes \boldsymbol{\eta}_1 \otimes \dots \otimes \boldsymbol{\eta}_N. \end{aligned}$$

If we consider the map $\Lambda_{th} = (\Gamma_{\mathbf{d}}^{-1} \otimes \mathbb{I}) \circ \Lambda \circ (\Gamma_{\mathbf{d}} \otimes \mathbb{I})$ (with the identity acting on the space of the auxiliary systems), it is easy to check that it is Gibbs-preserving, and it also maps $\mathbf{p}$ to $\mathbf{q}$ while correlating the auxiliary systems:

$$\begin{aligned} \Lambda_{th}(\mathbf{g} \otimes \boldsymbol{\eta}_1 \otimes \dots \otimes \boldsymbol{\eta}_N) &= \mathbf{g} \otimes \boldsymbol{\eta}_1 \otimes \dots \otimes \boldsymbol{\eta}_N, \\ \Lambda_{th}(\mathbf{p} \otimes \mathbf{c}_1 \otimes \dots \otimes \mathbf{c}_N) &= \mathbf{q}_\delta \otimes \mathbf{c}_{1,\dots,N}. \end{aligned}$$

Using Lemma 2.37, we can find a thermal process inducing the transformation above. Then, due to Proposition 2.36, we obtain 4. ■

3.3 Final remarks

3.3.1 Discussion

Comparing our Theorem 3.6 with Theorem 3.4 of [33], we can see that whenever a transformation is possible in the thermodynamic limit (i.e. when $\Delta F \leq 0$), then it is also possible by processing individual systems in the single-shot regime; what is needed is the creation of correlations among auxiliary systems whose local state is left unchanged. This is a surprising simplification of the thermodynamic ordering, compared to the infinite constraints $\Delta F_\alpha \leq 0$ of Theorem 3.3, and provides a non-asymptotic, operational meaning to the non-equilibrium free energy F .

It is useful to compare with recent results on work extraction from single quantum systems (see Fig. 3.6). The free energy F gives an absolute limit for the average amount of energy that can be extracted from single systems out of equilibrium. This bound is achievable but, when dealing with small and few systems, the work distribution can be very broad (Fig. 3.6, (1)). These fluctuations are a function of the initial non-equilibrium state and can be of the same order as the average extracted energy itself. Hence, arguably, the energy extracted can be more heat-like than work-like [46].

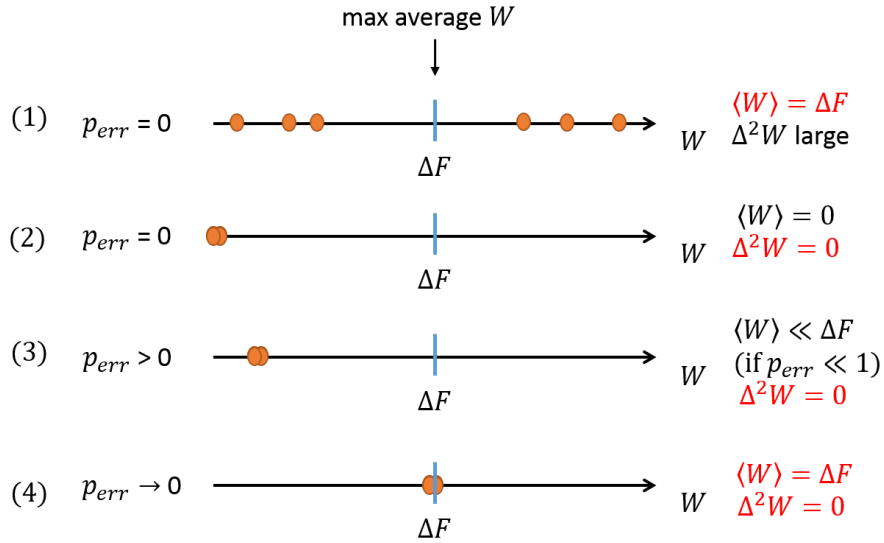


Figure 3.6. Extraction of work from out-of-equilibrium microscopic systems: ΔF is the limit for the average amount of work $\langle W \rangle$ that can be extracted, but the spread $\Delta^2 W$ can be very large (1). On the other hand, fluctuation-free, deterministic protocols generically yield zero work (2), unless an error probability $p_{err} > 0$ is introduced. However, for small errors, the average yield is much smaller than ΔF (3). Our protocol, exploiting stochastic independence, is fluctuation-free, has vanishing error probability and saturates the average work yield bound, i.e. $\langle W \rangle = \Delta F$ (4).

Since the ability to extract fluctuation-free work seems crucial for any engine that is trying to operate reliably in a non-equilibrium environment, fluctuation-free work extraction has been recently investigated in [23, 24]. It has been shown that from a system ρ incoherent in energy and with eigenvalues p we can deterministically extract work equal

to $F_0(\mathbf{p}) < F(\mathbf{p})$, with no fluctuations (this is a consequence of Theorem 3.3). However, it holds $F_0(\mathbf{p}) = 0$ for any full-rank state. As we can never ensure experimentally that a state does not have full rank, this immediately implies that strictly deterministic work extraction through Thermal Operations is practically impossible (Fig. 3.6, (2)); at best, the work yield will become tiny compared to $F(\mathbf{p})$ the smaller the failure probability we tolerate (Fig. 3.6, (3)). This is why the authors of [24] allow for some fixed (as opposed to arbitrarily small) error probability p_{err} in their model. With this probability, the protocol fails and no work is gained (actually, work is lost). Similarly does Åberg in his analysis [46]. Indeed, as Åberg's model shows, the role of the error probability is to focus on sufficiently likely energy levels of the system, a safeguard from unlikely but potentially harmful energy fluctuations.

The considerations above suggest that when performing work extraction at the nanoscale we either extract very little or no work, or we must include some large enough error probability p_{err} in the protocol. The twist of the present result is that neither of the two is necessary. Error-free, fluctuation-free work extraction from non-equilibrium systems is possible at optimal output $F(\mathbf{p}) - F(\mathbf{g})$ by creating correlations in the auxiliary systems used in the process (Fig. 3.6, (4)). From Theorem 3.6 it immediately follows that given ρ one can find auxiliary systems in a state $c_{1,\dots,N}$, $N \leq 3$, such that

$$\rho \otimes |0\rangle\langle 0| \otimes c_1 \otimes \dots \otimes c_N \rightarrow \gamma_S \otimes \chi_\epsilon(w) \otimes c_{1,\dots,N}, \quad (3.22)$$

where $w = F(\mathbf{p}) - F(\mathbf{g})$, and $\epsilon > 0$ can be chosen to be *arbitrarily* close to zero. Physically speaking, there is no difference between protocols ensuring an arbitrarily small error probability in the work bit $\chi_\epsilon(w)$ and a deterministic protocol that gives the pure excited state $|1\rangle$.

Also, notice that we only need to build up an arbitrarily small amount of correlations among the auxiliary systems, as measured by the mutual information. Indeed one can easily check from the non-increase of F in Eq. (3.22) that

$$\begin{aligned} F(\mathbf{p}) + \sum_i F(\mathbf{c}_i) &\geq F(\mathbf{g}) + (1 - \epsilon)w - kT_B H([\epsilon, 1 - \epsilon]) + F(\mathbf{c}_{1,\dots,N}) \\ &\implies I(\mathbf{c}_{1,\dots,N}) \leq H([\epsilon, 1 - \epsilon]) + \epsilon w / (kT_B), \end{aligned}$$

where I generalizes mutual information to N -partite systems (also known as total correlation):

$$I(\mathbf{c}_{1,\dots,N}) = S_1 \left(c_{1,\dots,N} \left\| \bigotimes_{i=1}^N c_i \right\| \right) = \sum_{i=1}^N H(\mathbf{c}_i) - H(\mathbf{c}_{1,\dots,N}).$$

Actually, an arbitrarily small $I(\mathbf{c}_{1,\dots,N})$ can be achieved for any transformation in this framework, not only for work extraction (see Aside 3.2).

Mathematical Aside 3.2. Arbitrarily small correlations for general transitions

Consider the statement of Theorem 3.6. We can always generate arbitrarily small amounts of correlations among the auxiliary systems.

Proof. Introduce an extra system in a thermal state γ_S , and consider the transformation $\rho \otimes \gamma_S \rightarrow \sigma \otimes \tau$, where τ is a state block-diagonal in the energy basis with eigenvalues t such that $F(t) = F(p) + F(g) - F(q)$. By construction, the free energy F of the left-hand-side equals the free energy of the right-hand-side, so Theorem 3.6 applies. Hence, for every $\epsilon > 0$, we can find $c_{1,\dots,N}$ with marginals $c_1, \dots, c_N$ and a Thermal Operation $\mathcal{T}_\epsilon$ such that $\mathcal{T}_\epsilon(\rho \otimes \gamma_S \otimes c_1 \otimes \dots \otimes c_N) = (\sigma \otimes \tau)_\epsilon \otimes c_{1,\dots,N}$, where $(\sigma \otimes \tau)_\epsilon$ is a state ϵ -close to $\sigma \otimes \tau$ in trace distance and with eigenvalues $(q \otimes t)_\epsilon$ such that $(q \otimes t)_\epsilon \xrightarrow{\epsilon \rightarrow 0} (q \otimes t)$. We can discard the extra system and obtain q_ϵ ϵ -close to q , due to the monotonicity of the trace distance under partial traces. Computing F on both sides of the previous equation, using the monotonicity of F and its additivity under tensor products, we obtain

$$I(c_{1,\dots,N}) \leq \frac{F(p) + F(g) - F((q \otimes t)_\epsilon)}{kT_B} = \frac{F(q \otimes t) - F((q \otimes t)_\epsilon)}{kT_B}.$$

From the continuity of F , it follows that $I(c_{1,\dots,N}) \xrightarrow{\epsilon \rightarrow 0} 0$. ■

3.3.2 Conclusions

The non-equilibrium free energy F is known to be relevant for the thermodynamics of a large number of uncorrelated systems [33]. This is not surprising, because $F(\rho) = \text{Tr}[\rho H_S] - kT_B S(\rho)$, and the von Neumann entropy S acquires its operational meaning in tasks involving infinitely many, identical states [26, 54]. However, we have shown here that F has a novel operational meaning for single-shot thermodynamics, i.e. for non-equilibrium, irreversible transformations on single systems.

An engine operating on correlated systems out of equilibrium will face extra irreversibility in comparison to the asymptotic or equilibrium regimes. For example, the amount of work w_{form} necessary to form a state exceeds the amount of work w_{ext} that can be extracted from it. This is because if ρ is a block-diagonal state with eigenvalues p , it follows from Theorem 3.3 and Eq. (2.32) (g being the Gibbs distribution)

$$\mathcal{T}(\rho \otimes |0\rangle\langle 0|) = \gamma_S \otimes |w_{\text{ext}}\rangle\langle w_{\text{ext}}| \Leftrightarrow w_{\text{ext}} \leq F_0(p) - F(g) = -kT_B \log \sum_{i|p_i \neq 0} g_i, \quad (3.23)$$

$$\mathcal{T}(\gamma_S \otimes |w_{\text{form}}\rangle\langle w_{\text{form}}|) = \rho \otimes |0\rangle\langle 0| \Leftrightarrow w_{\text{form}} \leq F_\infty(p) - F(g) = kT_B \log \max_i p_i / g_i. \quad (3.24)$$

and $F_\infty(p) \geq F_0(p)$ for all p [23, 24].³ However, Theorem 3.6 shows that an engine can operate at the reversible limit $w_{\text{form}} = w_{\text{ext}} = F$ if it can build up a small amount of correlations among few auxiliary systems. In principle, we can think of an engine oper-

³This can be seen as follows. Let j be the index of the maximum element among $\{p_i/g_i\}$. Then $\sum_{i|p_i \neq 0} p_i \frac{g_i}{p_i} \geq \min_{i|p_i \neq 0} \frac{g_i}{p_i} = \frac{g_j}{p_j}$. From this follows $\sum_{i|p_i \neq 0} g_i \geq \frac{p_j}{g_j} = 1 / \left(\max_i \frac{p_i}{g_i} \right)$.

ating on out-of-equilibrium microscopic systems and accessing a resource of “stochastic independence” (i.e. uncorrelated, auxiliary systems).

An interesting open question is the following: can we engineer typical (weak) system-environment interactions to generate the required correlations among the auxiliary systems? This would allow for a practical implementation of the engine. Moreover, are $N = 2$ auxiliary systems always enough? Can we give any bound on their sizes, as for standard catalysis [55]? One can show, for example, that a transition where F is constant can be performed creating an arbitrarily small amount of correlations only if the dimension of the auxiliary systems grows without bound (the proof of this fact is elementary but slightly cumbersome and can be found in [3], Appendix G).

A more difficult question is to ask what happens in the case in which the states are not block-diagonal in energy. A discussion of how to describe the thermodynamics of such systems will constitute the core part of the rest of this thesis, from Chapter 4 onwards.

It also seems worthwhile to look for concrete physical situations where local states c_i of large quantum systems, interacting with other systems in a heat bath, are forced to remain constant (say, due to local conservation laws). Our result suggests that there could be a tendency to build up correlations, similarly as there is a tendency to thermalize if the purity of the local states is allowed to decrease. This is particularly interesting due to the fact that the transition from product to correlated states is often regarded as an instance of an arrow of time.

Remark 3.12 (Open question). What are the consequences of these results for the resource theory of pure state entanglement, beyond standard catalysis studied in [25]? In particular, it seems that the decrease of von Neumann entropy of the reduced state is a sufficient condition for a LOCC to exist between two pure states, when aided by an ancillary system whose reduced state spectrum gets correlated. However, it is unclear what is the operational meaning of this scenario.

4 Thermodynamics beyond free energy

4.1 Introduction

Towards the lower-end of the nanoscale, quantum mechanical effects such as quantum coherence and entanglement increasingly make their presence felt. Electrical conductance of molecular-scale components no longer obey Kirchhoff's laws and phase coherence can provide both destructive as well as constructive interference effects on electrical transport [56]. Conversely, dissipative quantum thermodynamics offers the possibility of on-demand generation of quantum information resources essential for future quantum technologies (communication, encryption, metrology and computing) [57]. Within quantum information science, the question of thermodynamically robust quantum memories and thermodynamic constraints on quantum computation are still only partially understood and provide intriguing questions in the overlap between thermodynamics and quantum theory. In a similar way, the phenomenon of thermality due to entanglement reveals deep connections between thermodynamics and quantum information [7].

The physics of these remarkable small-scale systems, displaying coherence or entanglement, constitute extreme quantum scenarios. As such, a crucial question is: to what degree do traditional thermodynamic formulations and techniques encapsulate this regime? This is a broad, foundational question about thermodynamics. It is increasingly apparent that the traditional entropic formulation that emerges as an essentially unique description of the irreversibility of classical, macroscopic systems, will only place necessary, but not sufficient, constraints on the physics of small-scale systems manifesting coherence or quantum correlations.

The textbook treatments of classical, macroscopic equilibrium thermodynamics are typically based on notions such as Carnot cycles, with the entropy function generically defined via an integral in terms of heat flow [58]. This thermodynamic entropy function is then assumed (but often not proved) to completely describe the irreversible constraints on the system at hand. Alternative approaches follow a statistical mechanical treatment of the system based on underlying microstates, and provide an explanation of the thermodynamics in terms of microscopic degrees of freedom.

However, more rigorous derivations of the entropic form of the second law exist, such as by Carathéodory [59], Giles [14] and more recently by Lieb and Yngvason [15]. Of central importance is the partial order of thermodynamic states (see Chapter 2), from which an entropy function can then be derived in a rigorous manner. The existence of an essentially unique entropic form of the second law is found to be equivalent to highly

non-trivial assumptions on the structure of the thermodynamic partial order, such as the “Comparison Hypothesis” [14, 15]. Outside of the macroscopic classical regime, quantum systems will generically possess coherence or entanglement, and the ordering of states typically displays a much richer structure [30].

Since a unique additive entropic function implies that such assumptions must hold [15], their inapplicability in the quantum realm means that no single entropic function can suffice. To fully describe the thermodynamic directionality more than one entropy function is required, and Theorem 3.3 provides a clean characterization of non-asymptotic, thermodynamic interconversions of quantum states with zero coherence between energy eigenspaces. The necessary and sufficient conditions for such state interconversions are in terms of a set of entropic free energy functions ($\Delta F_\alpha \leq 0$). We now go beyond this, showing that even these fail to be sufficient for thermodynamic transformations involving non-zero quantum coherence.

Exploiting recent results in asymmetry theory (see Sec. 2.2.3), we show that thermodynamics can be viewed as being determined by at least two independent resources: the first is quantified by known free energies and measures how far a state is from being thermal; the second, a missing ingredient of previous treatments, measures how much a quantum state breaks time-translation invariance, i.e. the degree of quantum coherence in the energy eigenbasis present in the system. The theory of asymmetry provides *independent* thermodynamic relations ($\Delta A_\alpha \leq 0$, where A_α are measures of time-translation asymmetry) that are intrinsically quantum-mechanical in nature. This removes the “zero coherence” assumption made in numerous recent works, e.g. [3, 23, 24, 46, 60], and used extensively in the previous chapters.

This shift in perspective allows us to extend the free energy relations to a parallel set of thermodynamic constraints for quantum coherence. These laws restrict the set of possible thermodynamic transformations and characterize the tendency of any quantum state to “equilibrate” towards a time-symmetric state. The new relations, irrelevant for a system composed of many, uncorrelated bodies, become essential for the thermodynamics of small/correlated quantum systems. As an application, we show that in certain regimes the free energy splits into two components, one measuring the amount of classical free energy and the other measuring the quantum contribution coming from coherence. We show that coherence is not directly distillable as work, but does admit activation as a relational degree of freedom. We uncover a second form of fundamental irreversibility that parallels the one stressed in [24], but involves coherence transformations. Finally, we shed light on new connections between thermodynamics and entanglement theory.

Previous work considered either an asymptotic scenario or assumed the states to be block-diagonal in the eigenbasis of the Hamiltonian. Both these assumptions are insensitive to the role of coherence. Indeed, free energy relations are no longer sufficient for the single-shot thermodynamics of correlated and coherent quantum systems. As we shall see now, additional conditions are required due to the breakdown of time-translation invariance.

4.2 Time-asymmetry and Thermodynamics

Noether's theorem tells us that, if a system has time-translation invariance, then its energy is conserved. However, in general thermodynamic scenarios we have no time-translation invariance, either for the thermodynamic process on the system or for the quantum state of the system. The thermodynamics of a system generally involves irreversible dynamics and mixed quantum states out of equilibrium, and heat can flow into and out of the thermal reservoir.

One might therefore think that the unitary group generated by the free Hamiltonian H_S of the system should not play any particular role. However this is not the case, and from a perspective of asymmetry we find that (see also Fig. 4.1):

Theorem 4.1. *The set of Thermal Operations on a quantum system is a strict subset of the set of symmetric quantum operations with respect to time-translations, i.e. for $G = U(1)$.*

Proof. We need to prove that for any Thermal Operation $\mathcal{T}$ (see Eq. (2.48)):

$$\forall t, \quad \mathcal{T}(e^{-iH_S t} \rho e^{iH_S t}) = e^{-iH_S t} \mathcal{T}(\rho) e^{iH_S t}. \quad (4.1)$$

For any bath system $\gamma_B \propto e^{-\beta H_B}$, Eq. (4.1) follows using $[H_B, \gamma_B] = 0$ and $[U, H_S + H_B] = 0$:

$$\begin{aligned} \text{Tr}_B \left[U(e^{-iH_S t} \rho e^{iH_S t} \otimes \gamma_B) U^\dagger \right] &= \text{Tr}_B \left[U(e^{-iH_S t} \rho e^{iH_S t} \otimes e^{-iH_B t} \gamma_B e^{iH_B t}) U^\dagger \right] = \\ \text{Tr}_B \left[(e^{-i(H_S + H_B)t} U(\rho \otimes \gamma_B) U^\dagger e^{i(H_S + H_B)t}) \right] &= e^{-iH_S t} \text{Tr}_B \left[U(\rho \otimes \gamma_B) U^\dagger \right] e^{iH_S t}. \end{aligned}$$

That these operations form a proper subset is seen from the fact that shifting the energy of the system, while leaving the reservoir unchanged, is a symmetric operation, but not a thermally allowed operation. ■

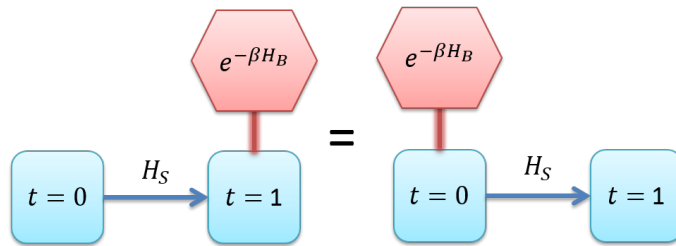


Figure 4.1. Time-translation symmetry. Connecting a thermal bath, with Hamiltonian H_B , to a quantum state before or after free time evolution does not make any difference to the resultant state. This simple symmetry implies laws that constrain the approach of a state to time-translation invariance.

As we will see, the implication of this result is that no thermodynamic process can generate additional time-translation asymmetry in the quantum system; since we will show that the G -twirling operation of Eq. (2.45) corresponds to complete dephasing in the energy eigenbasis (according to Def. 3.2), symmetric states correspond to states with no

superpositions among different energy levels. Non-increasing time-translation asymmetry is, then, a law of not increasing quantum coherence in the energy degrees of freedom.

A general picture emerges, where thermodynamics is governed by distinct abstract resources. The “thermodynamic purity” resource component, p , quantifies how ordered the state of the system is in the presence of a thermal bath, and its evolution is constrained by a set of free energy differences, as discussed in the previous chapters. If no quantum coherence is present, then consideration of p suffices; however, more generally, quantum thermodynamics is governed by the interplay of at least two fundamental resources, denoted by (p, a) . Free energy relations quantify the former, while asymmetry theory provides the tools to quantify the latter.

4.2.1 The incompleteness of existing second laws

We have shown that Thermal Operations are time-translation symmetric and argued that this requires consideration of coherence as a distinct thermodynamic resource. We now want to make this claim more precise and show that, in fact, no reasonable extension of the free energy “second laws” of Theorem 3.3 can properly account for the constraints characterising Thermal Operations. Put it another way, one may wonder if there is a generalisation of Theorem 3.3 of the form

$$\sigma = \mathcal{T}(\rho) \Leftrightarrow F(\rho) \geq F(\sigma) \quad \forall F \in \mathcal{F}, \quad (4.2)$$

where $\mathcal{F}$ is a family of generalised free energy functionals defined on the set of all quantum states. What we will prove now is that no such natural generalisation exists, if $\mathcal{F}$ has some minimal properties that all α -free energies share and that, arguably, are necessary to interpret $F \in \mathcal{F}$ as a free energy.

We now extract two core properties of free energy. The first is just a normalisation: given a family of free energy functionals $\mathcal{F}$ we require that

$$(P1) : \forall \rho, \quad \sup_{F \in \mathcal{F}} F(\rho) < +\infty.$$

For example, the α -free energies of Theorem 3.3 satisfy for $\alpha \geq 0$

$$F_\alpha(\mathbf{p}) \leq kT_B S_\infty(\mathbf{p}||\mathbf{g}) < +\infty, \quad (4.3)$$

where $\mathbf{g}$ is the Gibbs state.¹

The second property concerns the free energy of a battery system in an energy eigenstate $|w\rangle$ with energy w . For the α -free energies,

$$F_\alpha(|w\rangle\langle w|) = w, \quad (4.4)$$

¹For finite-dimensional systems, $S_\infty(\mathbf{p}||\mathbf{g}) = \log \max_i p_i/g_i < \infty$.

as one might expect from the fact that the state does not have any entropy content. More weakly, we require at least that the free energy of an infinite work source is infinite:

$$(P2) \quad \lim_{w \rightarrow \infty} F(|w\rangle\langle w|) = +\infty, \quad \forall F \in \mathcal{F}. \quad (4.5)$$

We can hence formulate the following:

Theorem 4.2 (Incompleteness through work). *Let $\mathcal{F}$ be a family of functionals satisfying properties (P1) and (P2). Then the conditions*

$$F(\rho) \geq F(\sigma), \quad \forall F \in \mathcal{F}, \quad (4.6)$$

are insufficient to ensure that there exists a Thermal Operation $\mathcal{T}$ with $\mathcal{T}(\rho) = \sigma$. If F are additive on independent systems, then this holds true even if we allow the use of catalysts.

Proof. First notice that, if we prove the rest of the theorem, the claim about catalysts follows immediately from the assumption of additivity of the measures.

Consider a system with a ladder Hamiltonian $H_S = \sum_{n>0} n |n\rangle\langle n|$. Let $\rho = |w\rangle\langle w|$ and $\sigma = |+\rangle\langle +|$, where $|+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$. Due to (P1), $\sup_{F \in \mathcal{F}} F(|+\rangle\langle +|) := f_+ < +\infty$. On the other hand, from (P2), for every F there exists w_F such that for all $w \geq w_F$ one has $F(|w\rangle\langle w|) > f_+$. Let $\bar{w} = \sup_F w_F$ ($\bar{w}$ may be infinite). Then in the transition

$$|\bar{w}\rangle\langle \bar{w}| \longrightarrow |+\rangle\langle +|, \quad (4.7)$$

all conditions of Eq. (4.6) are satisfied. However $A(\rho) = 0$, whereas $A(|+\rangle\langle +|) = \log 2$. Since A is monotonically decreasing under Thermal Operations, no Thermal Operation exists mapping the initial into the final state. Hence, the conditions of Eq. (4.6) are insufficient. ■

Another perspective is given by the following. Free energies can be increased arbitrarily by adding enough work. Hence classically, where free energies give sufficient conditions, work is a universal resource. Theorem 4.2 says that this is not the case quantum-mechanically. We will now see that for a thermodynamic transformation to be possible we need $A_\alpha(\rho) \geq A_\alpha(\sigma)$, for all $\alpha \geq 0$ and A_α measures of quantum coherence. In quantum thermodynamics, both the energetic and the coherent properties must be considered together. This is a major distinction from traditional thermodynamics, and leads us to a reconsideration of the entropic form of the second law from quantum mechanical systems.

4.2.2 Coherence Second Laws

We have shown that free energy relations are intrinsically deficient in capturing the features of quantum coherence in thermodynamics. We now present thermodynamic con-

straints that go beyond them. In particular we find that the core measures, used to define the generalized free energy relations of Theorem 3.3, can be extended in a natural way that provides asymmetry measures. We first need a notion of *quantum Rényi divergence*. Two distinct non-commutative extensions of the notion of α -Rényi divergence have been put forward [61, 62]. The operational interpretation in terms of hypothesis testing suggests to follow [63] in defining²

Definition 4.3 (Quantum Rényi divergences).

$$S_\alpha(\rho||\sigma) = \begin{cases} \frac{1}{\alpha-1} \log \text{Tr} [\rho^\alpha \sigma^{1-\alpha}], & \alpha \in (0, 1), \\ \frac{1}{\alpha-1} \log \text{Tr} \left[\left(\sigma^{\frac{1-\alpha}{2}} \rho \sigma^{\frac{1-\alpha}{2}} \right)^\alpha \right], & \alpha > 1. \end{cases}$$

The limit for $\alpha \rightarrow 1$ is given by $S_1(\rho||\sigma) = \text{Tr} [\rho(\log \rho - \log \sigma)] = S(\rho||\sigma)$. Also $\alpha \rightarrow 0, \infty$ are defined by suitable limits: denoting by Π_ρ the projector on the support of ρ ,

$$S_0(\rho||\sigma) = -\log \Pi_\rho \sigma, \quad S_\infty(\rho||\sigma) = \log \min\{\lambda : \rho \leq \lambda \sigma\}. \quad (4.8)$$

We now introduce the following notion:

Definition 4.4 (Free coherences). For any $\alpha \geq 0$ the *free coherence* of a state ρ with respect to a Hamiltonian H is

$$A_\alpha(\rho) := S_\alpha(\rho||D_H(\rho)),$$

where D_H is the operation that removes all coherence between energy eigenspaces (see Def. 3.2).

In the same way in which free energies measure “how far” a state is from being thermal, free coherences measure “how far” a state is from being incoherent in energy, i.e. time-translation invariant (see Fig. 4.2). For $\alpha \rightarrow 1$, we have $A_1(\rho) \equiv A(\rho)$ which is the asymmetry measure introduced in [40, 64, 65] (see also Lemma 2.44).³ With these definitions on board, and from Theorem 4.1, we immediately have the following result:

Theorem 4.5 (Coherence Second Laws). *Let H_S be the Hamiltonian of the system. For all $\alpha \geq 0$ we necessarily have $\Delta A_\alpha \leq 0$ for any Thermal Operation, or catalytic Thermal Operation with catalyst block-diagonal in energy.*

Proof. By assumption there exists some Thermal Operation $\mathcal{T}$ such that $\rho' = \mathcal{T}(\rho)$. Since $\mathcal{T}$ is a Thermal Operation, it is time-translation symmetric (Theorem 4.1). This can be

²Quantum Rényi divergences enjoy operational significance in state discrimination of two states ρ and σ , when a large number n of copies can be used. They give the exponent ξ of the decay in n of false positives ($\rho \neq \sigma$ even if they coincide), when the probability of false negatives (finding $\rho = \sigma$ even if the two states do not coincide) is assumed to decay exponentially in n with exponent r . With Def. 4.3, if $r < S(\rho||\sigma)$ then $\xi = \sup_{\alpha \in (0,1)} \frac{\alpha-1}{\alpha} [r - S_\alpha(\rho||\sigma)]$, whereas if $r > S(\rho||\sigma)$, then $\xi = \sup_{\alpha \in (1,+\infty)} \frac{\alpha-1}{\alpha} [r - S_\alpha(\rho||\sigma)]$ [63].

³In Chapter 6 we will see that $kT_B A_1(\rho) \equiv kT_B A(\rho)$ has an operational interpretation in terms of maximum average work that can be extracted from the coherence of a quantum state. This is the origin of the suggestive, if somehow not fully appropriate, name “free coherence”.

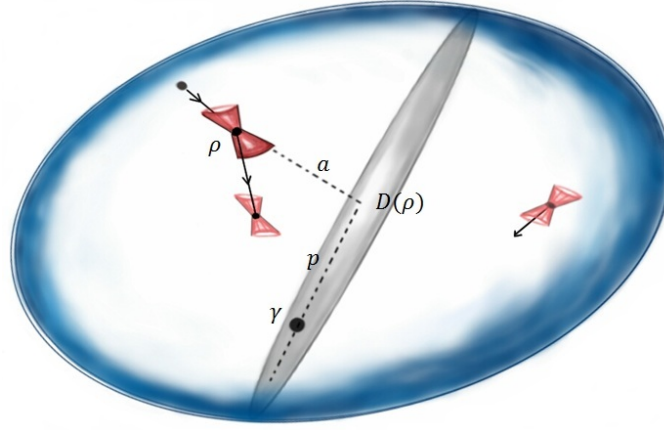


Figure 4.2. Quantum Thermodynamics as the combination of asymmetry and thermodynamic purity. The blue blob is the convex set of all quantum states. To any state ρ we can associate a “thermal cone” (in red), the convex set of states thermally accessible from it (and the backward cone of states that can access it). Any state ρ contributes in terms of thermodynamic purity p , which corresponds to the deviation – as measured by $\{F_\alpha\}$ – of $D_{H_S}(\rho)$ from the thermal state γ_S ; and asymmetry a , which corresponds to the deviation – as measured by $\{A_\alpha\}$ – of ρ from the manifold of time-symmetric states (the grey flat region).

written as

$$[\mathcal{T}, \mathcal{U}_t] = 0 \quad \forall t, \quad (4.9)$$

where $[\mathcal{T}, \mathcal{U}_t](\rho) = \mathcal{T}(\mathcal{U}_t(\rho)) - \mathcal{U}_t(\mathcal{T}(\rho))$. Note that we can write the dephasing operator as a group average

$$\mathcal{G}(\rho) = \int dt \mathcal{U}_t(\rho) = D_{H_S}(\rho), \quad (4.10)$$

where the integral is carried out on a suitably long interval and we used Eq. (2.45). Hence, using Eq. (4.9),

$$\mathcal{T} \circ D_{H_S}(\rho) = \int dt \mathcal{T}(\mathcal{U}_t(\rho)) = \int dt \mathcal{U}_t(\mathcal{T}(\rho)) = D_{H_S} \circ \mathcal{T}(\rho). \quad (4.11)$$

We will need to use the data processing inequality for the quantum Rényi divergences of Def. 4.3 [63, 63, 66–68]: for any quantum channel $\mathcal{E}$,

$$S_\alpha(\mathcal{E}(\rho) || \mathcal{E}(\sigma)) \leq S_\alpha(\rho || \sigma), \quad \forall \alpha \geq 0. \quad (4.12)$$

Then we obtain

$$A_\alpha(\mathcal{T}(\rho)) = S_\alpha(\mathcal{T}(\rho) || D_{H_S}(\mathcal{T}(\rho))) \stackrel{(4.11)}{=} S_\alpha(\mathcal{T}(\rho) || \mathcal{T}(D_{H_S}(\rho))) \stackrel{(4.12)}{\leq} S_\alpha(\rho || D_{H_S}(\rho)) = A_\alpha(\rho).$$

We now show that also catalytic Thermal Operations $\mathcal{C}$ with diagonal catalysts are symmetric operations on the system, so that $[\mathcal{C}, D_{H_S}] = 0$ and the same proof holds. Recall from Def. 3.1 that a state ρ is sent to ρ' through a catalytic Thermal Operation with

diagonal catalyst if there exists a system with Hamiltonian H_{cat} in a state σ , such that $[\sigma, H_{\text{cat}}] = 0$, and a Thermal Operation $\mathcal{T}$ with

$$\mathcal{T}(\rho \otimes \sigma) = \text{Tr}_3 \left[U(\rho \otimes \sigma \otimes \gamma_B) U^\dagger \right] = \rho' \otimes \sigma, \quad (4.13)$$

$$[U, H_T] = 0, \quad H_T = H_S + H_{\text{cat}} + H_B.$$

Here H_T is the sum of the Hamiltonians of system, catalyst and bath. Then, the quantum map $\mathcal{C}(\rho) = \text{Tr}_2 [\mathcal{T}(\rho \otimes \sigma)] = \rho'$ is symmetric. In fact, notice that $\sigma = e^{-iH_{\text{cat}}t} \sigma e^{iH_{\text{cat}}t}$, $\gamma_B = e^{-iH_Bt} \gamma_B e^{iH_Bt}$ for any t . It follows

$$\begin{aligned} \mathcal{C}(e^{-iH_S t} \rho e^{iH_S t}) &= \text{Tr}_2 [\mathcal{T}(e^{-iH_S t} \rho e^{iH_S t} \otimes \sigma)] = \text{Tr}_{23} \left[U(e^{-iH_S t} \rho e^{iH_S t} \otimes \sigma \otimes \gamma_B) U^\dagger \right] \\ &= \text{Tr}_{23} \left[e^{-iH_T t} U(\rho \otimes \sigma \otimes \gamma_B) U^\dagger e^{iH_T t} \right] = e^{-iH_S t} \text{Tr}_2 [\mathcal{T}(\rho \otimes \sigma)] e^{iH_S t} \\ &= e^{-iH_S t} \mathcal{C}(\rho) e^{iH_S t}. \end{aligned}$$

■

These laws characterize the depletion of coherence and the tendency to equilibrate onto the manifold of time-translation invariant states. Importantly, these provide constraints that are independent of any free energy relations, as we will discuss in the next section.

Remark 4.6 (Connections with fluctuation theorems). We can compare our framework with well-established results in non-equilibrium thermodynamics. Specifically, we compare with fluctuation theorem approaches [12, 69–71] that supply powerful descriptions of systems far from equilibrium. The standard description of the quantum version of such fluctuation theorems has significant limitations that are not present in our formalism. Firstly, while fluctuation theorems can be written down for quantum systems, they only capture stochastic effects which are “effectively classical” in nature. More specifically, the requirement of destructive measurements on the initial state unavoidably kills any coherence between energy eigenspaces, and unavoidably kills entanglement between systems. Attempts to generalize to positive operator valued measures (POVMs) quickly hit obstacles when it comes to the pairing of time-reversed trajectories. As such, only a limited set of quantum mechanical features can be currently addressed through fluctuation theorems.

Another possible route would be to focus on the expectation values of random variables – for example the outcomes of an energy measurement (as these in general will be sensitive to quantum coherence in the energy degrees of freedom). However it has been shown recently that even if you knew all the moments $\langle \hat{O}^k \rangle$ of a quantum observable $\hat{O}$, this is *insufficient* to describe the mixed state quantum mechanics of a system in the presence of a conservation law on $\hat{O}$ [45] (see box in Sec. 2.2.3).⁴ Intuitively, this is because e.g. the variance in energy may be both due to quantum coherence as well as classical

⁴One should be careful and notice that work, following the definition usually employed in fluctuation theorems, is not a quantum observable, because it is accessed by a two-points projective measurement.

mixedness, and these two distinct features cannot be told apart only by looking at the energy distribution [72]. Following these observations, a recent work appeared in the literature, taking an asymmetry theory point of view on fluctuation theorems [73].

4.2.3 Splitting of the free energy in classical and quantum components

The free energy F for $\alpha \rightarrow 1$ (see Def. 2.42) is the relevant measure of average work yield [74] – in what precise sense, it will be discussed extensively in Chapter 6. F naturally splits into a classical and a quantum contribution. Moreover, the two contributions to the quantum free energy must *independently* decrease under any thermodynamic process:

Theorem 4.7.

$$F(\rho) = F_c(\rho) + kT_B A(\rho), \quad (4.14)$$

where $A(\rho) = S(\rho||D_{H_S}(\rho))$ and $F_c(\rho) = F(D_{H_S}(\rho))$. Moreover, under any Thermal Operation

$$\Delta F_c \leq 0, \quad \Delta A \leq 0. \quad (4.15)$$

F_c is the “classical” free energy, i.e. the contribution to the free energy coming only from population and not from coherence among energy eigenspaces.

Proof. Summing and subtracting $kT_B S(D_{H_S}(\rho))$,

$$F(\rho) = \text{Tr}[H_S \rho] - kT_B S(D_{H_S}(\rho)) + kT_B (S(D_{H_S}(\rho)) - S(\rho)). \quad (4.16)$$

But from Eq. (4.10), $\mathcal{G}(\rho) = D_{H_S}(\rho)$. Then, as we have seen in the proof of Lemma 2.44,

$$\text{Tr}[\rho \log D_{H_S}(\rho)] = \text{Tr}[\rho \log D_{H_S}(D_{H_S}(\rho))] = \text{Tr}[D_{H_S}(\rho) \log(D_{H_S}(\rho))], \quad (4.17)$$

where we used that D_{H_S} is a projector and is hermitian, as well as the properties of the Hilbert-Schmidt scalar product. So,

$$S(D_{H_S}(\rho)) - S(\rho) = \text{Tr}[\rho \log \rho] - \text{Tr}[\rho \log D_{H_S}(\rho)] = S(\rho||D_{H_S}(\rho)) = A(\rho). \quad (4.18)$$

Substituting back into the first equation, using the definition of quantum free energy (Eq. (2.42)) and the fact that $\text{Tr}[H_S \rho] = \text{Tr}[H_S D_{H_S}(\rho)]$ we obtain Eq. (4.14).

Now let us prove the monotonicity claim. From Theorem 4.1, Thermal Operations are symmetric. Hence, from Lemma 2.44, A is monotonically decreasing under Thermal Operations. On the other hand, recall the expression $F(\rho) - F(\gamma_S) = kT_B S(\rho||\gamma_S)$ (where $S(\rho||\sigma) \equiv S_1(\rho||\sigma)$). Then,

$$\begin{aligned} F_c(\mathcal{T}(\rho)) - F(\gamma_S) &= kT_B S(D_{H_S} \circ \mathcal{T}(\rho)||\gamma_S) \stackrel{(4.11)}{=} kT_B S(\mathcal{T} \circ D_{H_S}(\rho)||\gamma_S) = \\ &\stackrel{(2.40)}{=} kT_B S(\mathcal{T} \circ D_{H_S}(\rho)||\mathcal{T}(\gamma_S)) \stackrel{(4.12)}{\leq} kT_B S(D_{H_S}(\rho)||\gamma_S) = F_c(\rho) - F(\gamma_S). \end{aligned}$$

■

Remark 4.8. What about coherences within each energy eigenspace? One can easily check that if $[U, H_S] = 0$ then $F(U\rho U^\dagger) = F(\rho)$. One can choose U such that it simultaneously diagonalises every energy block. So we see that F only depends on the eigenvalues of $D_{H_S}(\rho)$ and the coherence *among* energy eigenspaces.

Notice that a similar result, although differently interpreted, was found in the context of quantum reference frames [75].

4.2.4 Emergence of classicality

The second laws of coherence (Theorem 4.5) are not only relevant for the thermodynamics of a small number of quantum systems, but also at the macroscopic scale in the presence of correlated quantum systems able to sustain coherence. The regime in which the coherence second laws may be neglected is for systems composed of many, non-interacting bodies. We formalize this question and answer it, by showing that the free coherences per particle in a system of n non-interacting qubits vanish in the $n \rightarrow \infty$ limit:

$$\lim_{n \rightarrow \infty} A_\alpha(\rho^{\otimes n})/n = 0, \quad \forall \alpha \geq 0. \quad (4.19)$$

This generalizes the result found in [40] for $\alpha \rightarrow 1$ and describes an emergent classical scenario in which states become effectively time-symmetric. This is the reason why only the free energy governs the asymptotic behaviour in Theorem 3.4 of [33].⁵ In particular, the following bound holds

Theorem 4.9. *If ρ is a qubit system,*

$$0 \leq A_\alpha(\rho^{\otimes n}) \leq \log(n+1), \quad \forall \alpha \geq 0. \quad (4.20)$$

Mathematical Aside 4.1. Proof of Theorem 4.20

$A(\rho^{\otimes n}) \geq 0$ for every n holds due to the positivity of the α -relative entropies. Without loss of generality we can fix the Hamiltonian of the system to be the Pauli Z operator. Assume we are able to prove the result for every pure qubit state $|\psi\rangle$. Then for every ρ there exists p and $|\psi\rangle$ such that $\rho = p|\psi\rangle\langle\psi| + (1-p)\mathbb{I}/2 := \mathcal{E}_{mix}(|\psi\rangle\langle\psi|)$. Mixing with the identity is easily seen to be a time-translation symmetric operation: $\mathcal{E}_{mix}(e^{-iZt}\sigma e^{iZt}) = e^{-iZt}\mathcal{E}_{mix}(\sigma)e^{iZt}$ for all t . Hence we can map $|\psi\rangle\langle\psi|^{\otimes n} \rightarrow \rho^{\otimes n}$ by means of symmetric operations. However, A_α are monotones under symmetric operations, as follows from the proof of Theorem 4.5. So, $A_\alpha(|\psi\rangle\langle\psi|^{\otimes n}) \geq A_\alpha(\rho^{\otimes n})$, $\forall \alpha \geq 0$. We conclude that we need to prove the bound only for pure states and then the result will follow for any state. In fact, we will give an explicit expression for A_α on n copies of any qubit pure state.

⁵The theorem in [33] is given for transitions involving two general quantum states. A fine print is that an amount of quantum coherence sublinear in the number of systems involved is consumed.

Since rotations about Z are time-translation symmetric operations, all A_α are invariant under them (due to reversibility). Hence, without loss of generality, we can assume $\rho = |\psi\rangle\langle\psi|$, where $|\psi\rangle$ lies on the xz plane of the Bloch sphere:

$$\rho = \begin{bmatrix} p & \sqrt{p(1-p)} \\ \sqrt{p(1-p)} & 1-p \end{bmatrix} \quad (4.21)$$

Let us now have a look at the pattern:

$$\rho^{\otimes 2} = \begin{bmatrix} p^2 & p^{3/2}(1-p)^{1/2} & p^{3/2}(1-p)^{1/2} & p(1-p) \\ p^{3/2}(1-p)^{1/2} & p(1-p) & p(1-p) & p^{1/2}(1-p)^{3/2} \\ p^{3/2}(1-p)^{1/2} & p(1-p) & p(1-p) & p^{1/2}(1-p)^{3/2} \\ p(1-p) & p^{1/2}(1-p)^{3/2} & p^{1/2}(1-p)^{3/2} & (1-p)^2 \end{bmatrix},$$

It is useful to introduce a vector $|v_n\rangle$ whose elements are grouped in blocks as follows: 1 element equal to $\sqrt{p^n}$, $\binom{n}{1}$ elements equal to $\sqrt{p^{n-1}(1-p)}$, ..., $\binom{n}{h}$ elements equal to $\sqrt{p^{n-h}(1-p)^h}$, ..., 1 element equal to $\sqrt{(1-p)^n}$. Then we can compactly rewrite $\rho^{\otimes n} = |v_n\rangle\langle v_n|$. We will use the notation $D_{\sum_{i=1}^n Z_i} \equiv D$. Expanding in the computational basis,

$$D(\rho^{\otimes n}) = \bigoplus_{h=0}^n p^{n-h}(1-p)^h |\mathbb{I}_h\rangle\langle\mathbb{I}_h|, \quad |\mathbb{I}_h\rangle = \underbrace{(1, \dots, 1)}_{\binom{n}{h} \text{ elements}}. \quad (4.22)$$

Now let us focus on $\alpha \in (0, 1)$. Of course, $(\rho^{\otimes n})^\alpha = \rho^{\otimes n} = |v_n\rangle\langle v_n|$. Then define $P = D(\rho^{\otimes n})^{\frac{1-\alpha}{2}} |v_n\rangle\langle v_n| D(\rho^{\otimes n})^{\frac{1-\alpha}{2}}$. From the definition of A_α and the cyclic property of the trace,

$$A_\alpha(\rho^{\otimes n}) = \frac{1}{\alpha-1} \log \text{Tr} [P], \quad \text{for } \alpha \in (0, 1). \quad (4.23)$$

From $\langle\mathbb{I}_h|\mathbb{I}_h\rangle = \binom{n}{h}$, we have

$$(|\mathbb{I}_h\rangle\langle\mathbb{I}_h|)^{\frac{1-\alpha}{2}} = \binom{n}{h}^{\left(\frac{1-\alpha}{2}-1\right)} |\mathbb{I}_h\rangle\langle\mathbb{I}_h|,$$

so that, from Eq. (4.22),

$$D(\rho^{\otimes n})^{\frac{1-\alpha}{2}} = \bigoplus_{h=0}^n \binom{n}{h}^{-\frac{\alpha+1}{2}} [p^{n-h}(1-p)^h]^{\frac{1-\alpha}{2}} |\mathbb{I}_h\rangle\langle\mathbb{I}_h|.$$

Define $|w_n\rangle = D(\rho^{\otimes n})^{\frac{1-\alpha}{2}} |v_n\rangle$. Then $P = |w_n\rangle\langle w_n|$ and

$$|w_n\rangle = \bigoplus_{h=0}^n \binom{n}{h}^{-\frac{\alpha+1}{2}} [p^{n-h}(1-p)^h]^{\frac{1-\alpha}{2}} |\mathbb{I}_h\rangle\langle\mathbb{I}_h| |v_n\rangle.$$

The vector $|\mathbb{I}_h\rangle\langle\mathbb{I}_h| |v_n\rangle$ is also grouped in blocks $h = 0, 1, \dots, n$, each of $\binom{n}{h}$ equal elements. One of the elements of the h -block can be found as follows: the matrix of ones $|\mathbb{I}_h\rangle\langle\mathbb{I}_h|$ sums the elements in the h -block of $|v_n\rangle$ (which are $\binom{n}{h}$ and identical), getting $\binom{n}{h} \sqrt{p^{n-h}(1-p)^h}$. Adding the prefactors we see that the elements of the h -block of

$|w_n\rangle$ look like:

$$\binom{n}{h}^{-\frac{\alpha+1}{2}} [p^{n-h}(1-p)^h]^{\frac{1-\alpha}{2}} \binom{n}{h} p^{\frac{n-h}{2}} (1-p)^{\frac{h}{2}}.$$

We conclude

$$\langle w_n | = \left(1, \dots, \underbrace{\binom{n}{h}^{\frac{1-\alpha}{2}} [p^{n-h}(1-p)^h]^{\frac{2-\alpha}{2}}}_{\binom{n}{h} \text{ elements}}, \dots, 1 \right).$$

$$\langle w_n | w_n \rangle = \sum_{h=0}^n \binom{n}{h}^{2-\alpha} [p^n - h(1-p)^h]^{2-\alpha} = \|x(n)\|_{2-\alpha}^{2-\alpha}, \quad (4.24)$$

where

$$x(n) := \left\{ \binom{n}{0} p^n, \dots, \binom{n}{h} p^{n-h}(1-p)^h, \dots, \binom{n}{n} (1-p)^n \right\},$$

and we used the usual definition of ℓ^p -norm,

$$\|x\|_p = \left(\sum_i |x_i|^p \right)^{1/p}.$$

Hence,

$$A_\alpha(|\psi\rangle\langle\psi|^{\otimes n}) = \frac{2-\alpha}{\alpha-1} \log \|x(n)\|_{2-\alpha} = H_{2-\alpha}(\mathbf{x}), \quad (4.25)$$

that gives an explicit expression for the α -free coherence of $|\psi\rangle^{\otimes n}$. We can now use the following identity: for all $p > r > 0$, if y is a sequence of k elements, $\|y\|_r \leq k^{(\frac{1}{r}-\frac{1}{p})} \|y\|_p$. This gives $\|x(n)\|_{2-\alpha} \geq (n+1)^{\frac{1-\alpha}{2-\alpha}}$, from which we deduce

$$A_\alpha(\rho^{\otimes n}) \leq \log(n+1). \quad (4.26)$$

A similar calculation can be performed for $\alpha > 1$, along the lines presented in [5]. One needs some extra care: we can restrict the calculation to $\text{supp}[D(\rho^{\otimes n})] \supseteq \text{supp}[\rho^{\otimes n}]$. The final result is

$$A_\alpha(|\psi\rangle\langle\psi|^{\otimes n}) = H_{1/\alpha}(\mathbf{x}), \quad \forall \alpha > 1. \quad (4.27)$$

Using again the inequality above (with $p = 1$ and $r = 1/\alpha$), we get $A_\alpha(\rho^{\otimes n}) \leq \log(n+1)$ for $\alpha > 1$.

An alternative argument shows the result for arbitrary α . In [33] a formation protocol is presented in the asymptotic $n \rightarrow \infty$ limit that creates, from $\gamma_S^{\otimes n}$, n copies of an arbitrary qubit state ρ using a coherence resource ρ_R made of a uniform superposition over a number $2n^{2/3}$ of energy levels (plus work). Because every A_α is monotonically decreasing under Thermal Operations, this implies that $A_\alpha(\rho^{\otimes n}) \leq A_\alpha(\rho_R) \leq \log 2^{2n^{2/3}} \sim n^{2/3}$ (as every A_α is bounded by the logarithm of the Hilbert space dimension). This is sub-linear in n , so $A_\alpha(\rho^{\otimes n})/n \xrightarrow{n \rightarrow \infty} 0$.

We will use Theorem 4.20 shortly to study work extraction at the classical-quantum boundary.

4.3 Thermodynamic consequences of time-translation symmetry

4.3.1 Quantum Szilard: work is locked in coherences

The notions of work and heat are the primary concerns of thermodynamics, and with the advent of small-scale thermodynamics it has been necessary to revisit these time-honoured concepts (see, *e.g.*, [54, 60, 76–78] and references therein). The analysis of Szilard [79] showed that the information one has about a system has an energetic value in terms of the ordered work one can obtain from a disordered thermal reservoir at temperature T_B [80]. Specifically, the possession of a single bit of information can be “consumed” to obtain $kT_B \log 2$ Joules. More generally, let ρ be a state incoherent in the energy eigenbasis, with eigenvalues $\mathbf{p}$ and Hamiltonian H_S . Standard thermodynamic arguments imply that in the presence of a thermal reservoir at a fixed temperature we can obtain from ρ an average amount of work equal to $F(\mathbf{p}) - F(\mathbf{g})$, where $\mathbf{g}$ is the Gibbs distribution. Previous works [24, 60] have shown how to extend this result to deterministic and probabilistic work extraction from single quantum systems with zero coherence across energy eigenspaces (see Sec 3.3.2).

However, when we encounter quantum states containing coherences we must necessarily take into account constraints coming from time-translation symmetry. One might think that the work relations extend without alteration, but this is not the case – quantum coherences cannot be simply converted into ordered energy, and so the standard Szilard result must be modified. Consider a general, probabilistic work extraction:

$$\rho \otimes |0\rangle\langle 0| \rightarrow \sigma \otimes \sum_w p(w) |w\rangle\langle w|.$$

In this transformation the initial state ρ is left in some (partially) exhausted state σ ; the battery, with Hamiltonian $H_w = \sum_w w |w\rangle\langle w|$ and initially in the ground state $|0\rangle$, is potentially left in a mixed state.⁶ Given this, we have the following:

Theorem 4.10 (Work-locking). *The distributions $p(w)$ that can be obtained from the states ρ and $D_{H_S}(\rho)$ through Thermal Operations coincide.*

Proof. Suppose it is possible to obtain from ρ a distribution $p(w)$ through a Thermal Operation $\mathcal{T}$:

$$\mathcal{T}(\rho \otimes |0\rangle\langle 0|) = \sigma \otimes \sum_w p(w) |w\rangle\langle w|. \quad (4.28)$$

If we apply $\mathcal{T}$ to $D_{H_S}(\rho)$, it is easy to see from Eq.(4.11) and the previous equation that

$$\mathcal{T}(D_{H_S}(\rho) \otimes |0\rangle\langle 0|) = D_{H_S}(\sigma) \otimes \sum_w p(w) |w\rangle\langle w|, \quad (4.29)$$

so $p(w)$ can be achieved from $D_{H_S}(\rho)$ as well. Conversely, any distribution $p(w)$ that can

⁶Here we do not claim that $p(w)$ should be interpreted as work in every case (in fact, it should not). But we stress that the result holds independently of the interpretation attached to $p(w)$.

be achieved from $D_{H_S}(\rho)$ can also be obtained from ρ . In fact, the state $D_{H_S}(\rho)$ can be obtained from ρ through dephasing in energy, which is easily shown to be a Thermal Operation from Eq. (4.10) and the convexity of Thermal Operations (this will be proved formally in Lemma 5.10). Hence, any distribution that can be obtained from $D_{H_S}(\rho)$ can also be obtained from ρ . ■

This result was found for average work extraction in [81] and for deterministic work extraction in [24]. We now see that it is a consequence of the time-translation symmetry of Thermal Operations. This leads to a work-locking phenomenon, in which $D_{H_S}(\rho)$ and ρ have the same the same work value. This happens despite the fact that, for example, $F(\rho) > F(D_{H_S}(\rho))$ whenever ρ carries coherence among energy eigenspaces.⁷ The free energy contribution from coherence is locked. This puzzle will be the main object of investigation in Chapter 6, where we will show that if we are in possession of coherence resources work-locking can be partially removed – and in the limit of having a classical field at our disposal it disappears completely.

This also sheds light on the origin of the irreversibility noticed in [24]. On one hand the work necessary to form a state, measured by F_∞ , is bigger than the work that we can draw from it, given by F_0 , because $F_0 < F_\infty$ (see Sec. 3.3.2). This first irreversibility is not an intrinsically quantum phenomenon, as it is a sole consequence of the free energy constraints of Theorem 3.3. Indeed, this same irreversibility is present even for diagonal states (probability distributions) undergoing Thermal Operations (particular stochastic processes), a classical - albeit not deterministic - theory. However, quantum coherence adds another layer of irreversibility, as the work necessary to generate the coherent part of a quantum state cannot be extracted later, due to the fact that thermodynamic operations are time-translation symmetric quantum maps.

In the thermodynamic limit work-locking is undetectable. From Eqs. (4.14) and Theorem 4.20, we have that for a system of n qubits with local Hamiltonians H_i :

$$F(\rho^{\otimes n}) \approx F\left(D_{\sum_i H_i}(\rho^{\otimes n})\right), \quad (4.30)$$

when $n \gg \log n$. The free energy is effectively classical; moreover, since

1. From states with no quantum coherence in the energy eigenbasis one can extract an average amount of work equal to the free energy change ΔF in the state.
2. The quantum free energy is additive on tensor products,

the previous equation shows that the maximum average extractable work per system approaches $F(\rho) - F(\gamma_S)$ in the $n \rightarrow \infty$ limit, despite work-locking. In particular, using Theorem 4.20,

$$\frac{\langle W \rangle}{n} = \frac{F\left(D_{\sum_i H_i}(\rho^{\otimes n})\right) - F(\gamma_S)}{n} = F(\rho) - F(\gamma_S) - kT_B \frac{A(\rho^{\otimes n})}{n} \geq F(\rho) - F(\gamma_S) - kT_B \frac{\log(n+1)}{n}.$$

⁷This is clear from Theorem 4.7 and $A(\rho) = 0$ if and only if $\rho = D_{H_S}(\rho)$. The latter follows from the definition of A and the properties of the relative entropy.

In other words, the deficit scales as $\log n/n$.

Recovering the free energy in the resource theory framework

Many arguments, devised within different frameworks, highlight the special role of the quantum free energy $\alpha = 1$ in the context of average work extraction and asymptotic scenarios (see e.g. [46] for a particularly clean derivation). From a resource theory perspective, Theorem 3.4 ensures that for n large enough Thermal Operations can induce arbitrarily well the transformation

$$\rho^{\otimes n} \rightarrow |w\rangle\langle w|^{\otimes Rn}, \quad (4.31)$$

with $R = \Delta F(\rho)/\Delta F(|w\rangle\langle w|)$. There is here a small technicality to see the connection with standard results. This is due to the fact that we should answer the question: what is the work value we assign to each of the states $|w\rangle\langle w|$ we created? Using the results of the box in Sec. 3.1.2 (that can also be derived from the free energy second laws for incoherent states of Theorem 2.38), the work value of each copy of $|w\rangle\langle w|$ is $w + kT_B \log Z = \Delta F(|w\rangle\langle w|)$ (here Z is the partition function of the battery Hamiltonian). Hence, the average work extracted is

$$\langle W \rangle = \lim_{n \rightarrow \infty} \frac{1}{n} (Rn) \Delta F(|w\rangle\langle w|) = \Delta F(\rho), \quad (4.32)$$

as expected. As mentioned, this result holds for general states if we allow the injection of a sublinear amount of coherent systems; if everything we care about is their work content, their free energy is sublinear in n and hence nothing changes in the accounting made in the $n \rightarrow \infty$ limit. This already hints at questions we will ask in more detail in Chapter 6, regarding a proper accounting of the coherent resources consumed as well as the need to process n copies of the same state at a time.

A reference frames point of view on work-locking

Recall the discussion about reference frames in Sec. 2.2.3. Theorem 4.1 shows that Thermal Operations are time-translation symmetric. Hence, an agent restricted to Thermal Operations experiences in particular the same constraints of lacking a clock to measure time. As such, even if we are given a pure state $|\psi\rangle$, we cannot really distinguish it from any of the other elements in the orbit under time-translations, $\{e^{-iH_S t} |\psi\rangle\}$. Averaging over this ignorance is equivalent to dephasing in the energy basis. This is the reason for the appearance of work-locking and, moreover, it suggests how to try to overcome it: by introducing a reference frame for time, i.e., a system carrying quantum coherence in the energy eigenbasis. Conversely, it shows that results claiming work extraction from coherence are exploiting, explicitly or implicitly, coherent resources (typically, a classical field that acts as a classical reference frame). This naturally leads to the discussion about how to “activate” work using coherence resources.

4.3.2 Coherent activation of work

We have established that one must associate with a state both purity and asymmetry, abstractly denoted (p, a) , and have shown that coherences in isolation do not contribute to thermodynamic work. Schematically, if $(p, a) \rightarrow W$ then $(p, 0) \rightarrow W$ too. It might appear that quantum coherences have no effect on the work output of a thermodynamic process, but this is not the case.

In the case of states block-diagonal in the energy eigenbasis, any state that cannot be prepared under Thermal Operations can be converted into mechanical work. In the fully quantum-mechanical setting this is no longer the case. There are states that cannot be prepared through Thermal Operations from which it is impossible to draw any useful work. These are precisely the states ρ with coherence for which $D_{H_S}(\rho) = \gamma_S$. An extreme case is the pure state

$$|\gamma_S\rangle = Z_S^{-1/2} \sum_k e^{-\beta E_k/2} |E_k\rangle, \quad (4.33)$$

where $|E_k\rangle$ are the eigenstates of H_S and Z_S its partition function. However, while $(0, a) \rightarrow (W = 0)$, it turns out coherence can be activated in the presence of other quantum systems with coherence:

$$(0, a_1) + (0, a_2) \rightarrow (W \neq 0). \quad (4.34)$$

By $A + B \rightarrow C$ we mean it is possible to transform A and B jointly into C , using Thermal Operations only. Eq. (4.34) tells us the only way to extract on average an amount of work equal to the free energy F from a state like $|\gamma_S\rangle$ is to smuggle in coherent resources. Only if we allow the use of an external source of coherence does this extraction of work become possible (see Chapter 6).

The way in which coherence in a state ρ can be utilized to obtain mechanical work is readily seen from asymmetry theory and the theory of quantum reference frames [38]. Having shown that Thermal Operations commute with time-translation, all the results concerning work extraction under the presence of a superselection rule (e.g. [82]) can be immediately applied to thermodynamics. If we have *two* quantum systems with Hamiltonians H_1 and H_2 and respectively in states ρ_1 and ρ_2 for which $D_{H_1}(\rho_1) = \gamma_{S_1}$ and $D_{H_2}(\rho_2) = \gamma_{S_2}$ ($\gamma_{S_i} \propto e^{-\beta H_i}$), then individually no mechanical work can be obtained in the presence of a thermal reservoir. However the two systems can instead encode relational coherence that is accessible. Specifically, the introduction of the second system gives $D_H(\rho_1 \otimes \rho_2) = \sigma_{12} \neq \gamma_{S_1} \otimes \gamma_{S_2}$, where $H = H_1 \otimes \mathbb{I} + \mathbb{I} \otimes H_2$. This is also why collective actions on multiple copies can extract work in a situation in which operations on single copies would be useless [81].

Alternatively, we can distinguish one of the systems as being the dominant reference. This perspective admits a different physical interpretation. Denote by $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively, the Hilbert spaces where ρ_1 and ρ_2 live. Take the dimension of $\mathcal{H}_2$ to be much larger than $\mathcal{H}_1$, and the state ρ_2 to be highly asymmetric compared to ρ_1 (in what precise

	Quantum Thermodynamics	Entanglement Theory
Asymptotic conversion $\rho^{\otimes n} \rightarrow \sigma^{\otimes m}$	Rel. entropy [33] $F(\rho) = kT_B S(\rho \gamma_S)$	Rel. entropy [8] $\inf_{\sigma \in \mathcal{S}} S(\rho \sigma)$
$W \rightarrow (p, 0) \rightarrow W' < W$	Non-cyclicity [24]	Ent. formation $\neq$ Ent. distillation
$(p, a) \rightarrow W \leftarrow (p, 0)$	Work locking	Bound entanglement [83]
$(0, a_1) + (0, a_2) \rightarrow W$	Coherence activation	Entanglement activation [84]

Table 4.1. Quantum thermodynamics and entanglement manipulations structural parallels. The asymptotic interconversion of states are governed by relative entropy to the Gibbs states γ_S and the relative entropy to the manifold of separable states $\mathcal{S}$, respectively. The work necessary to create a state is bigger than the work extractable from it and similarly happens with entangled state creation and distillation. There are states that cannot be created under thermal (LOCC) operations from which no work (entanglement) can be extracted, but the resource can be activated.

sense, it will be discussed in Chapter 6). The function of ρ_2 is to allow the simulation of a non-symmetric operation $\tilde{\mathcal{E}}$ on the first system (see also [42]):

$$\tilde{\mathcal{E}}(\rho_1) = \text{Tr}_2[\mathcal{E}(\rho_1 \otimes \rho_2)] \quad (4.35)$$

The idea is to break time-reversal symmetry in the work system ρ_1 , exploiting the initial asymmetry of ρ_2 , for example to overcome work-locking.

4.4 Discussion

In [23, 24] the authors showed that the work needed to create a state ρ block-diagonal in energy is measured by $F_\infty(\rho)$ and the work extractable is given by $F_0(\rho)$ (see Sec. 3.3.2). This revealed an inherent irreversibility in the thermodynamic transformation. We can now show that a similar irreversibility characterizes the thermodynamic processing of coherence. While normally one wishes to distil out ordered energy via a thermodynamic process, we could equally ask to obtain a high degree of coherence in the final output state under the allowed quantum operations. One, for example, could wish to obtain a d -dimensional uniform superposition of energy states, $|\mathbb{I}(d)\rangle := d^{-1/2} \sum_k |k\rangle$. Conversely, we may want to know how much coherence is needed to create a quantum state. If σ_{sym} is some incoherent quantum state, the coherence second laws require

$$\begin{aligned} \rho \rightarrow \sigma_{sym} \otimes |\mathbb{I}(d_{out})\rangle\langle\mathbb{I}(d_{out})| &\Rightarrow \log d_{out} \leq A_0(\rho) \\ |\mathbb{I}(d_{in})\rangle\langle\mathbb{I}(d_{in})| \otimes \sigma_{sym} \rightarrow \rho &\Rightarrow \log d_{in} \geq A_\infty(\rho). \end{aligned}$$

which shows that a further, fundamental irreversibility affects coherence processing as at least $A_\infty(\rho) - A_0(\rho)$ amount of coherence is lost in a cycle.

Our results also shed light on the relationships between entanglement theory and thermodynamics [7, 8, 85] (see Table 1). Beyond structural parallels, this work also paves the way for an explicit unification of the resource theories presented here, and of the now well-developed theory of entanglement.

The resource-theoretic perspective is just one recent approach to the thermodynamics of quantum systems, however we argue that this framework presents an elegant and compact perspective on quantum thermodynamics in terms of the interconversion and quantification of the two abstract properties: thermodynamic purity and time-asymmetry. These seem to be necessary components in any unified framework that seeks to describe coherent processes, and generic quantum thermodynamic phenomenon with no classical counterpart.

Remark 4.11 (Open question). Does the creation of correlations help also in overcoming symmetry constraints? One could hope so, as the creation of correlations can “hide” local coherence, *e.g.* coherence can be created locally with energy-preserving transformations if correlations between systems are created [34]. We leave this open for future research.

5 Modes of coherence in thermodynamics

5.1 The paradigmatic setting

The central question of thermodynamics is: what are the allowed transformations of a system that are consistent with the first and second laws? We established in the previous chapter that quantum coherence *cannot* be properly described by free energy constraints, and that new and independent relations are required. These new constraints characterise general processes that conserve energy in the interaction with an incoherent environment; they were derived from the resource theory that quantifies the degree to which a quantum state lacks time-translation invariance.

Let us now set the scene with a transparent example that illustrates the issues at hand. The simplest possible example is a qubit system with Hamiltonian $H_S = |1\rangle\langle 1|$ that can interact with arbitrary heat baths at temperature $kT_B = \beta^{-1}$, through energy-conserving interactions on the composite system (these are Thermal Operations, see Sec. 2.2.2). The thermal state of the system is given by $\gamma_S = e^{-\beta H_S} / \text{Tr} [e^{-\beta H_S}]$. The core question now is: given a qubit state ρ that possesses quantum coherence, what is the set of quantum states $\mathcal{T}_\rho$ accessible from ρ under Thermal Operations? As will be clear from the general results of this chapter, and as can be seen from the qubit characterisation of Thermal Operations introduced in [86], its basic structure is that of a rotationally symmetric (about the Z-axis), convex set of states. In the X-Z plane of the Bloch sphere, this set is given by the dark red solid region and the orange triangle in Fig. 5.1. The boundary surface of the red region denotes the states that preserve the maximal amount of coherence while having a given final energy distribution. Let us analyse the structure of $\mathcal{T}_\rho$ in a more detailed way to show the non-triviality of coherence transformations in thermodynamics.

First of all, one might expect that, due to the intrinsically dissipative interactions of a quantum system with the heat bath, coherence is only playing a passive role in the process. If this was the case all possible transformations would be attainable just by a combination of dephasings and Thermal Operations on incoherent states. However

$$\mathcal{T}_\rho \supset \{\sigma | \sigma = \lambda \rho + (1 - \lambda) \mathcal{T}(D_{H_S}(\rho)), \lambda \in [0, 1], \mathcal{T} \text{ Thermal Operation}\}. \quad (5.1)$$

In fact, the set of states achievable without ever processing coherence in a non-trivial way (the right-hand-side of the previous equation) is limited to the orange triangle in Fig. 5.1 and clearly does not coincide with $\mathcal{T}_\rho$ (details will be given later). We conclude that coherence is actively contributing to enlarge the set of thermodynamically accessible

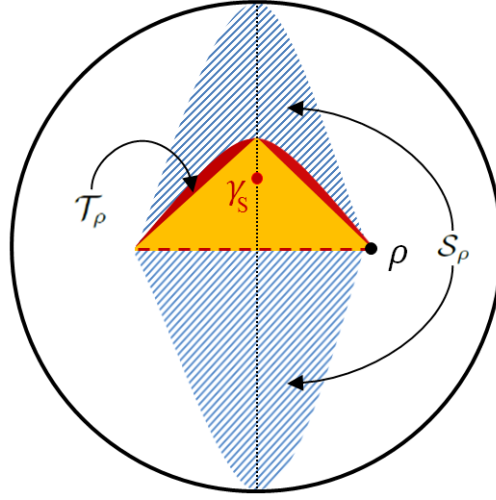


Figure 5.1. The basic structure. The set of states $\mathcal{T}_\rho$ achievable under Thermal Operations from the initial qubit state ρ is presented on the X-Z plane of the Bloch sphere. $\mathcal{T}_\rho$ (which is symmetric with respect to rotations about the Z axis) is given by the dark red solid region and the orange triangle (γ_S is the thermal state of the system). If Thermal Operations on coherent states were trivial, in the sense that they were equivalent to dephasings and operations on incoherent states, then this set would reduce to the orange triangle. Moreover, even if one has access to arbitrary amount of work (but not coherence), then the set of achievable state is extended to the dashed blue region $\mathcal{S}_\rho$, but not to the whole Bloch sphere.

states.

One might also ask the following question: if we are given an unbounded amount of free energy, would coherence still be a resource? If the answer was no, all constraints could be lifted by a sufficiently large work source. Work would be *the* universal resource of thermodynamics, as it is in the classical case. However, as we discussed in the previous chapter, this is not the case – and this is one reason why quantum thermodynamics is interesting. Now we can make that discussion even more precise. Suppose the unbounded amount of work is given in the form of an arbitrary number of copies of pure, zero-coherence states, say $|0\rangle^{\otimes N}$. Then

Theorem 5.1. *Consider the resource theory defined by the following free operations:*

1. *Thermal Operations,*
2. *Preparing ground states of the system Hamiltonian.*

Then, the set of allowed operations coincides with the set of time-translation symmetric maps.

Remark 5.2 (Work is not universal). Because the coherence second laws of Theorem 4.5 have been derived only using the fact that Thermal Operations are time-translation symmetric, we see that all coherence constraints remain valid even if an infinite work source is provided. Allowing infinite work only extends $\mathcal{T}_\rho$ to the set of states $\mathcal{S}_\rho$ accessible under “time-symmetric evolutions” (dashed blue region in Fig. 5.1), which is a strict subset

of the full Bloch sphere. Therefore, we can conclude that work is not a universal resource and coherence resources should be carefully accounted for.

Proof of Theorem 5.1. Denote by $|0\rangle$ the ground state of the system Hamiltonian. Thermal Operations are time-translation symmetric and $|0\rangle$ is a symmetric (incoherent) state. Hence, the set of allowed operations must be a subset of time-translation symmetric maps.

Conversely, any symmetric operation $\mathcal{E}$ possesses a Stinespring dilation [41]

$$\mathcal{E}(X) = \text{Tr}_E \left[U(X \otimes \sigma_E) U^\dagger \right], \quad (5.2)$$

where σ_E is a symmetric state, and U is a symmetric (i.e., energy-preserving) unitary on the joint system. U is clearly a Thermal Operation, so the only remaining question is if σ_E can be prepared by means of Thermal Operations using an infinite work source.

This can be seen by thinking about the effect of adding work on the thermo-majorisation curves [24]. Alternatively, notice that (due to Theorem 3.4) starting from an arbitrarily large number of $|0\rangle$ states and using Thermal Operations we can generate an arbitrarily good approximation of any incoherent state. Hence, all symmetric states can be produced. ■

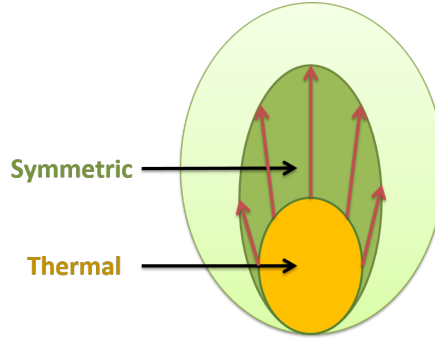


Figure 5.2. Thermodynamic and time-translation symmetry egg: adding an infinite work source extends the set of Thermal Operations (smaller orange blob) to the set of time-translation symmetric operations (green central blob). The larger, light green blob represents the set of all quantum channels. The figure neatly shows that the symmetry constraints introduced cannot be lifted by the addition of a work source; this illustrates their independence from the free energy constraints, that are trivialised by the addition of work.

Remark 5.3 (Symmetry reasoning goes beyond free energy). The theorem can be precisely summarised by saying that adding to Thermal Operations an infinite work source one gets the set of time-translation symmetric operations. This tells us something important when we couple it to the discussion of Sec 4.2.1: any reasonable set of constraints based on free energy functionals will be trivialised by an infinite work source. Hence, they cannot capture *any* of the constraints that are due to time-translation symmetry only. For

example, the quantum version of the second laws put forward in [23] has this limitation. This illustrates once more the importance of symmetry reasoning beyond free energy in thermodynamics.

5.2 Thermal Operations and Symmetries

5.2.1 Thermal operations

As observed before, we identify two main properties of Thermal Operations:

1. They are time-translation symmetric, i.e., as follows from Theorem 4.1,

$$\mathcal{T}(e^{-iH_S t} \rho e^{iH_S t}) = e^{-iH_S t} \mathcal{T}(\rho) e^{iH_S t}. \quad (5.3)$$

2. They preserve the Gibbs state, as seen in Eq. (2.40),

$$\mathcal{T}(\gamma_S) = \gamma_S. \quad (5.4)$$

The first property reflects energy conservation, a consequence of the first law, and the fact that the thermal bath is an incoherent mixture of energy states. The second property incorporates the core physical principle of the second law of thermodynamics: the non-existence of a machine able to run a cycle in which thermal energy is converted into work. Eq. (5.4) requires that we cannot bring a thermal state out of equilibrium at no work cost. In fact, unless further constraints do not allow us to equilibrate a state back and extract work, a violation of Eq. (5.4) would give us a perpetuum mobile of the second kind.

5.2.2 Modes of coherence

A time-covariant (i.e. time-translation symmetric) map can be decomposed according to its action on the *modes* of a state [42]. Denote the set of all differences between eigenfrequencies of H_S by $\{\omega\}$ (this is sometimes called “Bohr spectrum”). The system state $\rho = \sum_{x,y} \rho_{xy} |x\rangle\langle y|$ can then be written in the form

$$\rho = \sum_{\omega} \rho^{(\omega)}, \quad \rho^{(\omega)} := \sum_{\substack{x,y \\ \omega_x - \omega_y = \omega}} \rho_{xy} |x\rangle\langle y|. \quad (5.5)$$

The operators $\rho^{(\omega)}$ are called *modes of coherence* of the state ρ . Now, if $\mathcal{E}$ is a covariant operation such that $\mathcal{E}(\rho) = \sigma$,

$$\mathcal{E}(\rho^{(\omega)}) = \sigma^{(\omega)} \quad \forall \omega. \quad (5.6)$$

In other words, each mode $\rho^{(\omega)}$ of the initial state is independently mapped by a covariant operation to the corresponding mode $\sigma^{(\omega)}$ of the final state.¹ We can now conveniently parameterise a covariant map $\mathcal{E}$ in the following way. First, let us define the action of $\mathcal{E}$ on diagonal (i.e., mode zero) matrix elements by

$$\mathcal{E}(|x\rangle\langle x|) = \sum_{i=0}^{d-1} p_{x'|x} |x'\rangle\langle x'|, \quad (5.7)$$

where the coefficients are the entries $\Lambda_{x'x} = p_{x'|x}$ of a stochastic matrix Λ ($\Lambda_{x'x} \geq 0$ and $\sum_x \Lambda_{x'x} = 1$). This can be naturally interpreted as the transition matrix between energy eigenstates. The action of $\mathcal{E}$ on the off-diagonal matrix element $|x\rangle\langle y|$ belonging to a non-zero mode ω can be parametrised as follows:

$$\mathcal{E}(|x\rangle\langle y|) = \sum_{\substack{x',y' \\ \omega_{x'} - \omega_{y'} = \omega}} c_{y'|x}^{x'} |x'\rangle\langle y'|. \quad (5.8)$$

The coefficients $c_{y'|x}^{x'}$ parametrise how much the initial coherence $|x\rangle\langle y|$ contributes to the final coherence $|x'\rangle\langle y'|$. Hermiticity of the final state imposes $c_{y'|x}^{x'} = (c_{x'|y}^{y'})^*$. Note that formally $p_{x'|x}$ can be thought of as $c_{x'|x}^{x'}$.

As an example we now look at a qubit system, that without loss of generality can be described by the Hamiltonian $H_S = |1\rangle\langle 1|$.

Example 5.4. The state ρ can be decomposed into three modes consisting of the following matrix elements:

$$\begin{aligned} \rho^{(0)} &: \{|0\rangle\langle 0|, |1\rangle\langle 1|\}, \\ \rho^{(1)} &: \{|1\rangle\langle 0|\}, \\ \rho^{(-1)} &: \{|0\rangle\langle 1|\}. \end{aligned}$$

As a covariant map does not mix modes, the action of $\mathcal{E}$ on ρ is given by

$$\begin{aligned} \mathcal{E}(|0\rangle\langle 0|) &= p_{0|0} |0\rangle\langle 0| + p_{1|0} |1\rangle\langle 1|, \\ \mathcal{E}(|1\rangle\langle 1|) &= p_{1|1} |1\rangle\langle 1| + p_{0|1} |0\rangle\langle 0|, \\ \mathcal{E}(|1\rangle\langle 0|) &= c_{0|0}^{1|1} |1\rangle\langle 0|, \\ \mathcal{E}(|0\rangle\langle 1|) &= c_{1|1}^{0|0} |0\rangle\langle 1|. \end{aligned}$$

Since $p_{1|0} = 1 - p_{0|0}$, $p_{0|1} = 1 - p_{1|1}$ and $c_{0|0}^{1|1} = (c_{1|1}^{0|0})^*$, a general covariant qubit map is fully specified by two transition probabilities, $p_{0|0}$ and $p_{1|1}$, and a complex number $c_{1|1}^{0|0}$.

Note that these constraints are only due to the symmetry properties of Thermal Opera-

¹Covariance implies $\mathcal{E}(\rho^{(\omega)}) = e^{i\hbar\omega t} \mathcal{U}_t \circ \mathcal{E}(\rho^{(\omega)})$, where $\mathcal{U}_t = e^{-iH_S t}(\cdot)e^{iH_S t}$. Integrating over t , $\mathcal{E}(\rho^{(\omega)}) = \int dt e^{i\hbar\omega t} \mathcal{U}_t \circ \mathcal{E}(\rho^{(\omega)})/N$, for some normalisation N . But $P_\omega \propto \int dt e^{i\hbar\omega t} \mathcal{U}_t$ is a projector on mode ω , from which it follows that $\mathcal{E}(\rho^{(\omega)}) = \sigma^{(\omega)}$, where $\mathcal{U}_t(\sigma^{(\omega)}) = e^{-i\hbar\omega t} \sigma^{(\omega)}$.

tions, and therefore would hold in a situation where we allow arbitrary amounts of work to be available, as previously discussed. For a second non-trivial example, the modes of a qutrit systems with two equally spaced gaps are illustrated in Fig. 5.3.

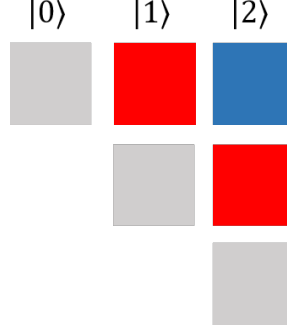


Figure 5.3. Qutrit modes. The coherence modes in the density matrix of a qutrit system with Hamiltonian $H_S = |1\rangle\langle 1| + 2|2\rangle\langle 2|$. The grey elements denote the zero mode $\rho^{(0)}$, that transforms trivially under time-translations. The red elements are mode one, $\rho^{(1)}$, satisfying $e^{-iH_S t} \rho^{(1)} e^{iH_S t} = e^{-it} \rho^{(1)}$ and the blue element is mode two, satisfying $e^{-iH_S t} \rho^{(2)} e^{iH_S t} = e^{-2it} \rho^{(1)}$. Finally, two other modes are not depicted: $\rho^{(-1)} = \rho^{(1)\dagger}$ and $\rho^{(-2)} = \rho^{(2)\dagger}$. As the state is Hermitian, without loss of generality one can consider positive modes only.

Thermo-majorization as a zero mode constraint

Necessary and sufficient conditions for thermodynamic interconversion between states block-diagonal in the energy eigenbasis are given by thermo-majorisation (Theorem 2.38).

Thermal Operations, being time-translation symmetric, satisfy Eq. (5.5). Consider the zero-mode constraint,

$$\mathcal{T}(\rho^{(0)}) = \sigma^{(0)}, \quad (5.9)$$

$\rho^{(0)}$ and $\sigma^{(0)}$ are quantum states, and they are both block-diagonal in energy. Hence, Theorem 2.38 applies and one has

$$\rho^{(0)} \succ_g \sigma^{(0)}, \quad (5.10)$$

where by the notation above we mean that the eigenvalues of $\rho^{(0)}$ thermo-majorise the eigenvalues of $\sigma^{(0)}$.

Eq. (5.6) shows that given two general quantum states, ρ and σ , for σ to be thermally accessible from ρ , a set of equations must be simultaneously fulfilled, one for each $\omega \in \{\omega\}$. The thermo-majorization condition of Eq. (5.10) only ensures that Eq. (5.6) is satisfied for $\omega = 0$, leaving open the question of the thermodynamic constraints on coherent transformations on all nonzero modes.

Incompleteness of the coherence constraints, or why we must use modes

Is this mode description really needed? We now show that such analysis is a necessary ingredient for thermodynamics and goes beyond Theorem 4.5. In fact, the proof of the coherence second laws only relied on the contractivity of the α -relative entropy under quantum channels and the fact that Thermal Operations commute with dephasing, see Eq. (4.11). However, the latter only corresponds to Eq. (5.6) for $\omega = 0$, i.e., it only requires that the zero mode of a state is mapped into itself and is hence blind to all conditions $\omega > 0$. These impose further restrictions on how coherence is transformed under Thermal Operations (such as the impossibility of mixing different modes) that we now describe.

5.3 Bounds on coherence preservation

The conceptual framework just described provides a natural way to analyse coherence within thermodynamics. We now develop both upper and lower bounds on how the modes of coherence evolve under general thermodynamic transformations.

5.3.1 Optimal coherence preservation

Time-translation symmetry condition

We will begin investigating the following question: given that a covariant map $\mathcal{E}$ transforms the diagonal elements of ρ according to the stochastic matrix Λ [see Eq. (5.7)], how much coherence can be preserved? Let $\sigma = \mathcal{E}(\rho)$; then formally for any given x', y' we are interested in $\max_{\mathcal{E}} |\sigma_{x'y'}|$, subject to $\mathcal{E}$ being covariant and $\mathcal{E}(|x\rangle\langle x|) = \sum_{x'} p_{x'|x} |x'\rangle\langle x'|$. In physical terms, we can think of this problem as follows: if we know the classical action of $\mathcal{E}$, i.e., the energy flows that it induces, how much coherence can be preserved? We will express the off-diagonal matrix elements of ρ in terms of their magnitudes and phase factors as $\rho_{xy} = |\rho_{xy}| \vartheta_{xy}$. The symbol $\sum_{x,y}^{(\omega)}$ will indicate a sum over all indices x, y such that $\omega_x - \omega_y = \omega$.

Theorem 5.5. *Let $\mathcal{E}$ be a covariant map such that $\sigma = \mathcal{E}(\rho)$, and whose classical action is given by the stochastic matrix Λ with elements $\Lambda_{x'x} = p_{x'|x}$. Then $|\sigma_{x'y'}|$ is bounded as*

$$|\sigma_{x'y'}| \leq \sum_{x,y}^{(\omega_{x'y'})} \sqrt{p_{x'|x} p_{y'|y}} |\rho_{xy}|, \quad (5.11)$$

where $\omega_{x'y'} = \omega_{x'} - \omega_{y'}$. All coherence terms can simultaneously attain the bound if there exists a set of phase factors $\{\phi_x\}$ such that

$$\forall_{x,y} \quad \vartheta_{xy} = \phi_x \phi_y^*. \quad (5.12)$$

Proof. The complete positivity of $\mathcal{E}$ is equivalent to the positivity of the Choi operator $J[\mathcal{E}]$ [87, 88]. However, $J[\mathcal{E}]$ satisfies $e^{-i\tilde{H}t} J[\mathcal{E}] e^{i\tilde{H}t} = J[\mathcal{E}]$, where $\tilde{H} = H_S \otimes \mathbb{I} - \mathbb{I} \otimes H_S^*$

(see Ref. [89], Eqs. (18)-(19)). This can be seen as follows: for any unitary U , $\mathcal{U} \otimes \mathcal{U}^*(\Omega) = \Omega$ if Ω is the maximally entangled state and $\mathcal{U}(\cdot) = U(\cdot)U^\dagger$. This can be readily checked from $\Omega = |\text{vec}(\mathbb{I})\rangle\langle\text{vec}(\mathbb{I})|/d$ and using the properties of vectorisation. Taking $U = e^{-iH_S t}$ we obtain

$$[\mathcal{U}_t \circ \mathcal{E} \circ \mathcal{U}_t^\dagger \otimes \mathcal{I}](\Omega) = [\mathcal{U}_t \circ \mathcal{E} \otimes \mathcal{I}](\mathcal{I} \otimes \mathcal{U}_t^*)(\Omega) = \mathcal{U}_t \otimes \mathcal{U}_t^*[\mathcal{E} \otimes \mathcal{I}](\Omega). \quad (5.13)$$

This immediately implies (using that J is an isomorphism)

$$\mathcal{U}_t \circ \mathcal{E} \circ \mathcal{U}_t^\dagger = \mathcal{E} \Leftrightarrow \mathcal{U}_t \otimes \mathcal{U}_t^* J[\mathcal{E}] = J[\mathcal{E}]. \quad (5.14)$$

$\mathcal{E}$ is covariant if and only if $J[\mathcal{E}]$ is symmetric with respect to the Hamiltonian $H_S \otimes \mathbb{I} - \mathbb{I} \otimes H_S^*$.

Hence, the Choi state is block diagonal in the eigenbasis of $\tilde{H}$ and the positivity of $J[\mathcal{E}]$ is equivalent to positivity of each block. Recall from the definition of the Choi state and Eq. (5.8) that

$$J[\mathcal{E}] = \sum_{x,y} \sum_{x',y'}^{(\omega_{xy})} c_{y'|y}^{x'|x} |x'\rangle\langle y'| \otimes |x\rangle\langle y| = \sum_{x',x} \sum_{y',y}^{(\omega_{x'x})} c_{y'|y}^{x'|x} |x'x\rangle\langle y'y|, \quad (5.15)$$

where we have rearranged the expression to emphasise the block-diagonal structure. Each block consists of matrix elements $c_{y'|y}^{x'|x}$ for which $\omega_{x'} - \omega_x = \omega_{y'} - \omega_y = \omega$ and can thus be labelled by ω . A necessary condition for the positivity of block ω is that for all x, y and x', y' within the block one has

$$|c_{y'|y}^{x'|x}| \leq \sqrt{p_{x'|x} p_{y'|y}}. \quad (5.16)$$

Then, from Eq. (5.8), $\sigma_{x'y'} = \sum_{x,y}^{(\omega_{x'y'})} c_{y'|y}^{x'|x} \rho_{xx'}$; by the triangle inequality and Eq. (5.16) we obtain the result claimed in Eq. (5.11).

We now proceed to prove the attainability of the bound. By choosing each block ω of the Choi state to be an unnormalised pure state $|\psi_\omega\rangle\langle\psi_\omega|$, where

$$|\psi_\omega\rangle = \sum_{x',x}^{(\omega)} \varphi_{x'x}^{(\omega)} \sqrt{p_{x'|x}} |x'x\rangle \quad (5.17)$$

and $\varphi_{x'x}^{(\omega)}$ is a phase factor, we ensure its positivity for any given classical action Λ . The corresponding quantum channel is given by $\mathcal{E}(\cdot) = \sum_\omega K_\omega(\cdot) K_\omega^\dagger$ with Kraus operators

$$K_\omega = \sum_{x',x}^{(\omega)} \varphi_{x'x}^{(\omega)} \sqrt{p_{x'|x}} |x'\rangle\langle x|. \quad (5.18)$$

One can check that these Kraus generate a time-translation symmetric channel with ma-

trix elements $c_{y'|y}^{x'|x}$ given by

$$c_{y'|y}^{x'|x} = \varphi_{x'x}^{(\omega)} \varphi_{y'y}^{(\omega)*} \sqrt{p_{x'|x} p_{y'|y}}. \quad (5.19)$$

The bound is achieved if we have $\varphi_{x'x}^{(\omega)} \varphi_{y'y}^{(\omega)*} = \vartheta_{xy}^*$.

Let us now use assumption $\vartheta_{xy} = \phi_x \phi_y^*$. Then the choice

$$\varphi_{x'x}^{(\omega)} = \phi_x, \quad \varphi_{y'y}^{(\omega)} = \phi_y^*, \quad \forall \omega \quad (5.20)$$

saturates the bound Eq. (5.11) simultaneously for all coherence terms $\sigma_{x'y'}$ (note that x and ω fix x' , due to the lack of degeneracy in H_S , and the same for y and ω with y'). ■

Remark 5.6. The condition specified in Eq. (5.12) that allows simultaneous saturation of the bound for all coherence terms is, in particular, satisfied by pure states ρ , as well as states with no phase factors in the energy eigenbasis.

Example 5.7. The three qubit modes identified in Example 5.4 correspond to blocks of the Choi state $J[\mathcal{E}]$ spanned by $\{|00\rangle, |11\rangle\}$, $\{|10\rangle\}$ and $\{|01\rangle\}$:

$$J[\mathcal{E}] = \frac{1}{2} \begin{pmatrix} p_{0|0} & c_{1|1}^{0|0} & 0 & 0 \\ \left(c_{1|1}^{0|0}\right)^* & p_{1|1} & 0 & 0 \\ 0 & 0 & 1 - p_{0|0} & 0 \\ 0 & 0 & 0 & 1 - p_{1|1} \end{pmatrix}.$$

The optimal coherence preservation thus reads

$$|\sigma_{10}| \leq \sqrt{p_{1|1} p_{0|0}} |\rho_{10}|,$$

and, since there is only a single coherence term, the bound can be attained (note that bounds for the negative modes are always redundant due to hermiticity). The Kraus operators that saturate the bound are given by:

$$K_0 = \sqrt{p_{0|0}} |0\rangle\langle 0| + \sqrt{p_{1|1}} |1\rangle\langle 1|, \\ K_1 = \vartheta_{10}^* \sqrt{1 - p_{0|0}} |1\rangle\langle 0|, \quad K_{-1} = \vartheta_{01}^* \sqrt{1 - p_{1|1}} |0\rangle\langle 1|.$$

Gibbs-preserving condition

The bound (5.11) can be refined further by noting that the Gibbs-preserving condition (5.4) puts restrictions on the transition probabilities $p_{l|k}$. Specifically, it induces the following equality:

$$\Lambda \mathbf{g} = \mathbf{g}, \quad (5.21)$$

where $\mathbf{g} = (g_0 \dots g_{d-1})$ denotes the vector of thermal probabilities of the d -dimensional system under consideration and Λ is the matrix whose elements $p_{l|k}$ are defined by Eq. (5.7). From (5.21) one can prove the following

Lemma 5.8. *Let Λ be a stochastic matrix with elements $p_{l|k}$ and satisfying $\Lambda \mathbf{g} = \mathbf{g}$. Then,*

$$p_{l|k} \leq e^{\beta \hbar (\omega_k - \omega_l)} \quad \forall_{k,l}. \quad (5.22)$$

Proof. From Eq. (5.21) after simple transformations one obtains that, for every l ,

$$p_{l|l} = 1 - \sum_{i \neq l} p_{l|i} \frac{g_i}{g_l}.$$

Taking into account that $p_{l|l}$ is positive (as it represents a transition probability), this yields for every $k \neq l$

$$p_{l|k} \leq \frac{g_l}{g_k} - \sum_{i \neq l,k} p_{l|i} \frac{g_i}{g_k} \leq \frac{g_l}{g_k} = e^{\beta \hbar (\omega_k - \omega_l)}.$$

■

Hence, if the energy of the final state $\hbar \omega_l$ is higher than the energy of the initial state $\hbar \omega_k$, the transition probability is bounded by $e^{-\beta \hbar (\omega_l - \omega_k)}$. Then,

Theorem 5.9 (Coherence preservation under Thermal Operations). *Let $\sigma = \mathcal{T}(\rho)$, where $\mathcal{T}$ is a Thermal Operation. Then, for all x', y' such that $\omega_{x'} - \omega_{y'} = \omega$,*

$$|\rho'_{x'y'}| \leq \sum_{\substack{x,y \\ \omega_x < \omega_{x'}}}^{(\omega_{x'y'})} |\rho_{xy}| e^{-\beta \hbar (\omega_{x'} - \omega_x)} + \sum_{\substack{x,y \\ \omega_x \geq \omega_{x'}}}^{(\omega_{x'y'})} |\rho_{xy}|. \quad (5.23)$$

Proof. Let us split the bound (5.11):

$$|\rho'_{x'y'}| \leq \sum_{\substack{x,y \\ \omega_x < \omega_{x'}}}^{(\omega_{x'y'})} \sqrt{p_{x'|x} p_{y'|y}} |\rho_{xy}| + \sum_{\substack{x,y \\ \omega_x \geq \omega_{x'}}}^{(\omega_{x'y'})} \sqrt{p_{x'|x} p_{y'|y}} |\rho_{xy}|.$$

where we used the time-translation symmetry condition $\omega_{x'} - \omega_{y'} = \omega_x - \omega_y$, that implies $\omega_{x'} - \omega_x = \omega_{y'} - \omega_y$. We can use the inequality (5.22) in the first sum and a trivial bound on the second sum. This gives the result. ■

This bound on coherence transformations by Thermal Operations can be easily interpreted physically. Time-translation symmetry implies that the contributions to $\rho'_{x'y'}$ can only come from elements within the same mode. The Gibbs-preserving condition (necessary for the non-existence of perpetual mobiles) imposes an asymmetry in the contributions to the final coherence. The initial low-energy coherences, when contributing

to the final high-energy coherences, are exponentially damped by the factor $e^{-\beta\hbar(\omega_{x'} - \omega_x)}$. On the other hand, our bound does not constrain the possibility of transforming high-energy coherences into coherences between lower energy levels. This irreversibility of coherence transformations can be best understood through elementary coherence manipulations, presented in Section 5.4. These bounds are very simple to compute given the initial state and the spectrum of the system Hamiltonian.

5.3.2 Guaranteed coherence preservation

Consider an initial state ρ , whose energy measurement statistics is given by the spectrum of $\rho^{(0)}$. Suppose we want to modify this to a state with energy distribution given by the spectrum of some $\sigma^{(0)}$. From Eq. (5.10) this is possible if and only if $\sigma^{(0)} \prec_g \rho^{(0)}$. The question is now: how much quantum coherence can be preserved in this process? Here we will establish a lower bound on the guaranteed coherence for such a transformation that relies only on known results about thermodynamic transformations among incoherent states [24] and the convexity of the set of Thermal Operations:

Lemma 5.10. *The set of TOs is convex.*

Proof. Let $\mathcal{E}_i, i = 1, 2$ be the Thermal Operations

$$\mathcal{E}_i(\rho) = \text{Tr}_{B_i} \left[U_i(\rho \otimes \gamma_{B_i}) U_i^\dagger \right], \quad (5.24)$$

where $\gamma_{B_i} = \frac{e^{-\beta H_i}}{Z_i}$ and $[U_i, H_S + H_i] = 0$. We now show that a linear combination

$$p\mathcal{E}_1 + (1 - p)\mathcal{E}_2, \quad (5.25)$$

is a Thermal Operation. Let us introduce a d -dimensional ancillary bath state γ_A with Hamiltonian $H_A = \mathbb{I}_d$ and a joint unitary acting on system, the two environments and the ancilla. The total Hamiltonian of this joint system is $H = H_S + H_1 + H_2 + H_A$. Now define the controlled unitary

$$U := U_1 \otimes \Pi_1 + U_2 \otimes \Pi_2, \quad (5.26)$$

where Π_1 and Π_2 are respectively rank k , and rank $d - k$ projectors onto the degenerate bath system of the ancilla A and $\Pi_1 + \Pi_2 = \mathbb{I}_d$. We can check that, for $i = 1, 2$,

$$\begin{aligned} [U_i \otimes \Pi_i, H] &= [U_i \otimes \Pi_i, H_S + H_i] \\ &= [U_i, H_S + H_i] \otimes \Pi_i = 0, \end{aligned}$$

so that $[U, H] = 0$. We finally have

$$\begin{aligned}\mathcal{E}(\rho) &= \text{Tr}_{E_1, E_2, A} \left[U(\rho \otimes \gamma_1 \otimes \gamma_2 \otimes \gamma_A) U^\dagger \right] \\ &= \frac{1}{d} \sum_{i=1}^2 \text{Tr}_{E_i, A} \left[U_i \otimes \Pi_i(\rho \otimes \gamma_i \otimes \mathbb{I}_d) U_i^\dagger \otimes \Pi_i \right] \\ &= \frac{k}{d} \mathcal{E}_1(\rho) + \left(1 - \frac{k}{d} \right) \mathcal{E}_2(\rho).\end{aligned}$$

Thus $\mathcal{E}$ defines a Thermal Operation equivalent to any rational convex combination of $\mathcal{E}_1$ and $\mathcal{E}_2$. Irrational convex combinations are approached with arbitrary accuracy. ■

Assume that there exists a Thermal Operation mapping $\rho^{(0)}$ into $\sigma^{(0)}$. Define Σ as the set of quantum states with a distribution over the energy eigenstates given by $\sigma^{(0)}$ and denote by $\mathcal{T}_\rho$ the set of states accessible from ρ through Thermal Operations. It is easy to see that $\Sigma \cap \mathcal{T}_\rho \neq \emptyset$, because the dephasing operation $\rho \mapsto \rho^{(0)}$ is a Thermal Operation. Hence, it is natural to ask which state in this intersection has the highest amount of coherence?

First consider the set $\mathcal{T}_{\rho^{(0)}}$, which is contained in $\mathcal{T}_\rho$ and is completely characterized by thermo-majorization through Theorem 2.38. Within this set, consider the states along the line of $\rho^{(0)}$ and $\sigma^{(0)}$, i.e.

$$\{\xi^{(0)} \in \mathcal{T}_{\rho^{(0)}} : \exists \lambda \in [0, 1] \text{ with } \sigma^{(0)} = \lambda \rho^{(0)} + (1 - \lambda) \xi^{(0)}\}. \quad (5.27)$$

From any of these we can define a state (see Fig. 5.4),

$$\sigma = \lambda \rho + (1 - \lambda) \xi^{(0)}. \quad (5.28)$$

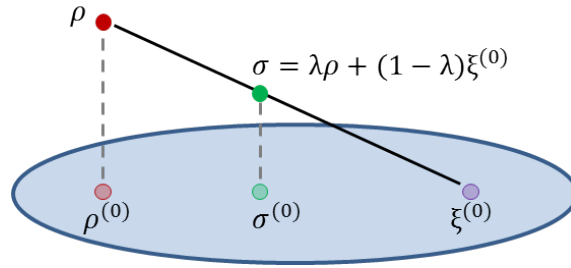


Figure 5.4. Guaranteed coherence. The shaded region represents the set of incoherent states. By convexity of the set of Thermal Operations, if $\xi^{(0)}$ is thermally achievable from $\rho^{(0)}$, then also σ can be achieved from ρ .

By construction $\sigma \in \Sigma$ and σ is a convex combination of two states in $\mathcal{T}_\rho$ ($\rho \in \mathcal{T}_\rho$ trivially and by definition $\xi^{(0)} \in \mathcal{T}_{\rho^{(0)}} \subseteq \mathcal{T}_\rho$). Because the set of Thermal Operations is convex, also $\mathcal{T}_\rho$ is convex. This immediately implies $\sigma \in \mathcal{T}_\rho$.

Now note that the modes $\sigma^{(\omega)}$ of the final state σ can only come from the initial state ρ , as $\xi^{(0)}$ has zero coherence. Therefore, we conclude that the fraction λ gives a lower

bound on the coherence that can be preserved in each mode, as $\sigma^{(\omega)} = \lambda \rho^{(\omega)}$. In other words, any $\xi^{(0)}$ will give us a value of λ that, in turn, gives a lower bound on how much coherence we can preserve in a thermodynamic transition from the initial state ρ into a final state with population given by $\sigma^{(0)}$. Our construction ensures

$$\exists \mathcal{T}(\rho) = \sigma : \mathcal{T}(\rho^{(0)}) = \sigma^{(0)} \text{ and } \sigma^{(\omega)} \geq \lambda \rho^{(\omega)}. \quad (5.29)$$

Sometimes it may be possible to extremize $\xi^{(0)}$ within the set $\mathcal{T}_{\rho^{(0)}}$ to obtain the highest possible fraction λ_* . Remarkably, as we will explicitly see in the next section, even this optimised bound is not tight already in the simplest scenario of a qubit system. Notice, from a physical perspective, that the guaranteed coherence bound is obtained by studying the set of states that can be achieved by the identity operation, complete dephasings, general transformations on incoherent states and convex combination of these; the fact that the bound is not tight when optimising over all such processes shows that the optimal coherence preservation necessarily needs Thermal Operations that process coherence in a non-trivial manner. This justifies the observations made in the introduction of this chapter.

5.3.3 Qubit scenario

The general arguments put forward in the previous section are now explicitly analysed for qubit systems.

Optimal coherence preservation for covariant and thermal maps

Let us first parametrize the initial state of the qubit system ρ and its final state σ , written in the eigenbasis of the Hamiltonian, in the following way

$$\rho = \begin{pmatrix} p & c \\ c & 1-p \end{pmatrix}, \quad \sigma = \begin{pmatrix} q & d \\ d & 1-q \end{pmatrix},$$

where c and d are assumed real without loss of generality, as a phase change in the coherence terms is both symmetric and conserves energy. The bound (5.16) for symmetric operations yields

$$d \leq c \sqrt{p_{0|0} p_{1|1}}. \quad (5.30)$$

To obtain a distribution $\mathbf{q} = (q, 1-q)$ from $\mathbf{p} = (p, 1-p)$ the transition matrix Λ , defined by transition probabilities $p_{j|i}$ with $i, j \in \{0, 1\}$, must fulfil $\Lambda \mathbf{p} = \mathbf{q}$. This condition together with the stochasticity of Λ gives

$$\begin{aligned} p_{0|0} &= \frac{(p_{1|1} - 1)(1-p) + q}{p} \leq \frac{q}{p}, \\ p_{1|1} &= \frac{(p_{0|0} - 1)p + 1 - q}{1-p} \leq \frac{1-q}{1-p}. \end{aligned}$$

Note that for $q < p$ only the first inequality is nontrivial, whereas for $q > p$ only the second inequality is non-trivial. Using these conditions in Eq. (5.30) gives:

$$d \leq \sqrt{\alpha}c, \quad \alpha = \min\left(\frac{q}{p}, \frac{1-q}{1-p}\right) \quad (5.31)$$

One can check that the time-translation symmetric CPTP map given by the following Kraus operators:

$$\begin{aligned} M_1 &= |0\rangle\langle 0| + \sqrt{\alpha}|1\rangle\langle 1|, \\ M_2 &= \sqrt{1-\alpha}|0\rangle\langle 1|, \end{aligned}$$

saturates this bound for $q > p$, whereas a CPTP map given by $\{X M_1 X, X M_2 X\}$, with $X = |0\rangle\langle 1| + \text{h.c.}$, saturates the bound for $q < p$. Of course if we can saturate the bound, we can also obtain all states with coherence smaller than maximal, simply by partially dephasing the optimal final state (partial dephasing is a symmetric operation). This shows that the bound of Eq. (5.31) captures all the constraints imposed by time-translation symmetry on the evolution of qubit states (a question left open in [45]). In Fig. 5.5 we depict the extremal set of achievable states via symmetric dynamics on a Bloch sphere for exemplary initial states (blue dot-dashed lines).

We will now focus on thermal maps and see how the condition $\Lambda \mathbf{g} = \mathbf{g}$, where $\mathbf{g} = (g, 1-g)$, changes the picture in thermodynamics. The choice of p and q , together with the Gibbs-preserving condition, completely fixes Λ :

$$\begin{aligned} p_{0|0} &= \frac{q(1-g) - g(1-p)}{p-g}, \\ p_{1|1} &= \frac{g(1-q) - p(1-g)}{g-p}. \end{aligned}$$

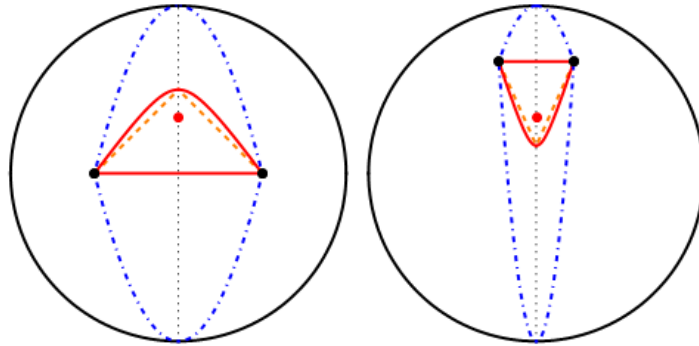


Figure 5.5. Time-translation invariance and thermodynamics in qubit systems. Extremal achievable states from a given initial state ρ (black points) under time-translation invariant (blue dot-dashed lines) and thermal (solid red lines) operations presented on a Bloch sphere. Dotted vertical lines join the eigenstates of system Hamiltonian and the red points correspond to the thermal occupation of the ground state, here chosen to be $g = 2/3$. Dashed orange lines give a triangle that corresponds to the set of states obtained using the bound for guaranteed coherence preservation.

Hence, from Eq. (5.30) we obtain

$$d \leq c \frac{\sqrt{(q(1-g) - g(1-p))(p(1-g) - g(1-q))}}{|p-g|}. \quad (5.32)$$

The above bound has been recently shown to be tight [86], i.e., there exists a Thermal Operation that saturates it. In Fig. 5.5 we depict the extremal set of obtainable states via Thermal Operations on the Bloch sphere for exemplary initial states (red solid lines). The range of achievable q given p was found solving the thermo-majorisation constraints. We will show how this is explicitly done in the next subsection, where we derive the guaranteed coherence bound.

Guaranteed coherence

Let us now proceed to the guaranteed coherence bound. Using the thermo-majorization condition for a qubit we find the extremal achievable incoherent states. In this simple qubit example this is achieved by the incoherent state as far as possible “on the other side” of the Gibbs-distribution. Let $\tilde{\mathbf{q}} = (\tilde{q}, 1 - \tilde{q})$ be the population of such extremal state. Then

$$\tilde{q} = 1 - \frac{1-g}{g}p. \quad (5.33)$$

This can be seen as follows. Let $\mathbf{g} = (g, 1-g)$ be the thermal distribution of the system. We can assume $p \neq g$, otherwise the situation is trivial (we cannot change this population). If $p < g$, then $q > g$ and the beta ordered probabilities are $(1-p, p)$ and $(q, 1-q)$. Then for the thermo-majorisation curve of the final state to be below that of the initial we need $\frac{q}{g}(1-g) \leq 1-p$, that gives $q \leq 1 - \frac{1-g}{g}p$. On the other hand, if $p > g$ then $q < g$ and we need $\frac{p}{g}(1-g) \leq 1-q$, that gives again $q \leq 1 - \frac{1-g}{g}p$. Hence, the extremal $\tilde{q}$ is that of the previous equation.

Using the previous result and Eq. (5.28), we find that the extremal state is characterised by

$$\lambda_* = \frac{q - \tilde{q}}{p - \tilde{q}}.$$

So we find that the maximal amount of coherence that can be preserved while transforming ρ into σ satisfies

$$d \geq \lambda_* c = \frac{q - \tilde{q}}{p - \tilde{q}} c = \left(1 - \frac{p-q}{p-g}g\right) c \quad (5.34)$$

This is a lower bound on the maximum amount of coherence that is possible to preserve in a thermodynamic transformation that changes the initial population $\mathbf{p} = (p, 1-p)$ into the final population $\mathbf{q} = (q, 1-q)$. The set of states obtained using the bound for guaranteed coherence preservation is depicted in Fig. 5.5 (orange dashed lines). The comparison with the achievable optimal bounds shows this is not tight even for qubits, as already anticipated.

In Fig. 5.6 we compare the set of achievable final states from a given initial state for

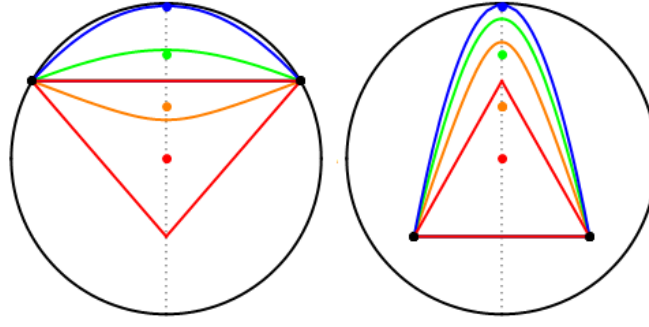


Figure 5.6. Qubit thermodynamics at various temperatures. Extremal achievable states from a given initial state ρ (black points) under Thermal Operations at different temperatures (colorful lines) presented on a Bloch sphere. Dotted lines join the eigenstates of system Hamiltonian and different colors correspond to different thermal occupations. The points on the Z axis represent thermal states for the same set of temperatures (the red point in the centre corresponds to infinite-temperature bath, whereas the blue one at the boundary corresponds to the low-temperature limit bath).

different thermal distributions, i.e., for different temperatures. We make two interesting observations concerning the thermal dependence of coherence preservation. Firstly, note that as g approaches 1 (the temperature goes to zero, which is the limit recently studied in [91]) the set of states obtainable via Thermal Operations coincides with “half” of the set of states obtainable via time-translation symmetric operations - the half for which $q > p$. This suggests that the limitations of low-temperature thermodynamics can be inferred from the limitations on symmetric operations, so from the resource theory of asymmetry. Secondly, let us distinguish between heating processes (when $q < p$) and cooling processes (when $q > p$). Then one can check that in the heating scenario the higher the temperature of the bath, the more coherence one can preserve, whereas for cooling processes, the lower temperature ensures better coherence preservation. This shows that for general thermodynamic state transformations to optimally preserve coherence it is necessary to use baths of different temperatures.

5.4 Applications to coherence transfer

Previous works on coherence transformations under Thermal Operations [86, 91] have made the simplifying assumption that all energy differences in the Hamiltonian of the system are distinct. However, it is only the overall coherence in a mode (the sum of coherence terms) that has to decrease, not each off-diagonal term separately. Therefore, previous results do not capture all the physics of ubiquitous systems such as harmonic oscillators or spin- j particles in a magnetic field, where modes are composed of more than one off-diagonal element. Our framework is suited to go beyond this restriction and reveals that within a given mode non-trivial dynamics takes place. However, thermodynamics imposes directionality on coherence transfers.

To introduce these features it suffices to consider the simplest system with non-trivial mode structure – a qutrit in a state ρ described by the following Hamiltonian:

$$H_S = \sum_{n=0}^2 n\hbar\omega_0 |n\rangle\langle n|.$$

Using Eq. (5.5) we easily identify that the mode ω_0 is composed of two off-diagonal elements:

$$\rho^{(\omega_0)} = \rho_{10} |1\rangle\langle 0| + \rho_{21} |2\rangle\langle 1|,$$

while, e.g., $\rho^{(2\omega_0)} = \rho_{20} |2\rangle\langle 0|$ consists of a single term (see also Fig. 5.3). We consider some primitive operations on this mode that may be used as building blocks in general coherence processing for higher-dimensional systems. One of them is *coherence shifting*: shifting up or down in energy the coherence between two given energy levels, preserving as much of it as we can (e.g. ρ_{10} can be shifted “up” to ρ_{21} , which can be then shifted “down” to ρ_{10}). Another primitive is *coherence merging*: given two coherence terms (e.g. ρ_{10} and ρ_{21}) one wants to optimally merge them into a single one (e.g. ρ_{10}). We will first study the limitations imposed by time-translation symmetry and then show how the situation changes in thermodynamics due to the second law.

5.4.1 Coherence shifting under Thermal Operations

Assume that the only non-vanishing coherence term is $|\rho_{10}| = c$ and that we want to transfer it inside mode ω_0 to $|\rho_{21}|$, i.e., we want to transform the coherence between energy levels $|0\rangle$ and $|1\rangle$ into coherence between $|1\rangle$ and $|2\rangle$. Our bound (5.16) for symmetric operations gives:

$$|\rho'_{21}| \leq c\sqrt{p_{1|0}p_{2|1}} \leq c. \quad (5.35)$$

If (5.35) is tight, a perfect shift can be obtained. It is easy to check that this is actually the case: a symmetric map described by Kraus operators

$$M_1 = |1\rangle\langle 0| + |2\rangle\langle 1|, \quad (5.36a)$$

$$M_2 = |2\rangle\langle 2|, \quad (5.36b)$$

perfectly shifts the coherence from $|1\rangle\langle 0|$ to $|2\rangle\langle 1|$. The situation would be analogous if we started with a coherence term $|\rho_{21}|$ and wanted to move it down in energy to $|\rho_{10}|$. Therefore, coherence transfer of a single mode element through symmetric operations is completely reversible.

This reversibility breaks down in thermodynamics, where the second law requires Eq. (5.4) to hold. We need to distinguish two situations: either we start with a coherence term $|\rho_{10}| = c$ and we move it up in energy to $|\rho_{21}|$ or we perform the reverse task. From Eq. (5.23) we immediately obtain a bound for the final magnitude of the transferred

coherence:

$$|\rho'_{10}| \leq c, \quad \text{for shifting down,} \quad (5.37a)$$

$$|\rho'_{21}| \leq ce^{-\beta\hbar\omega_0}, \quad \text{for shifting up.} \quad (5.37b)$$

Also in this case these bounds are tight, i.e., there are Thermal Operations achieving the above limits (see Fig. 5.7).

Proof. In both cases (moving the coherence term up and down in energy) we can use a bath state given by

$$\gamma_B = \frac{1}{Z} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega_0} |n\rangle\langle n|,$$

with partition function $Z_B = (1 - e^{-\beta\hbar\omega_0})^{-1}$. Now, consider the following joint unitary:

$$U = |0\rangle\langle 0| \otimes |0\rangle\langle 0| + (|0\rangle\langle 1| + |1\rangle\langle 2|) \otimes \Delta + |2\rangle\langle 0| \otimes \Delta^{2\dagger} + |1\rangle\langle 0| \otimes |0\rangle\langle 1|, \quad (5.38)$$

where $\Delta = \sum_{k=0} |k+1\rangle\langle k|$. Using $\Delta^\dagger \Delta = \mathbb{I}$ and $\Delta \Delta^\dagger = \mathbb{I} - |0\rangle\langle 0|$ one can check that U is unitary. It is easy to see that the above unitary is energy conserving, as it only mixes states with the same total energy. By direct calculation we can now check that

$$\begin{aligned} \text{Tr}_B \left[U(|2\rangle\langle 1| \otimes \gamma_B) U^\dagger \right] &= \text{Tr}_B \left[\Delta \gamma_B \Delta^\dagger \right] |1\rangle\langle 0| = |1\rangle\langle 0|, \\ \text{Tr}_B \left[U^\dagger(|1\rangle\langle 0| \otimes \gamma_B) U \right] &= \text{Tr}_B \left[\Delta^\dagger \gamma_B \Delta \right] |2\rangle\langle 1| = e^{-\beta\hbar\omega_0} |2\rangle\langle 1|. \end{aligned}$$

Hence both bounds, for shifting down in energy (Eq. (5.37a)) and up in energy (Eq. (5.37b)), are achievable via the Thermal Operations presented. ■

This proves that the irreversibility (directionality) within each mode suggested by Eq. (5.37b) as compared to Eq. (5.35) is not just an artefact due to the bounds being not tight. It is actually possible to perfectly transfer coherence down in energy, whereas the opposite task is exponentially damped due to the second law. Fig. 5.7 presents a “shift cycle”, in which coherence between high energy levels is transferred down to lower energies and then up again. Due to the second law this thermodynamic process is irreversible.

Remark 5.11 (Work and reversibility of coherence shifts). From Theorem 5.1, Thermal Operation plus an infinite work source allow to perform a generic time-translation invariant operation. From the results of this section this means that, in principle, coherence shifting can be made arbitrarily close to reversible by adding enough work into the process.

Remark 5.12 (Open question). What is the relation between the work added to the system and the reversibility of the induced coherent process? I.e. how much work does one need to invest to guarantee a given threshold level of reversibility?

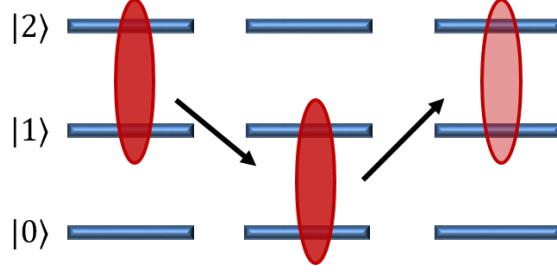


Figure 5.7. Irreversibility of coherence shift cycle. Coherence between high energy levels is transferred down to low energy levels and then up again. The magnitude of the coherence terms is proportional to the intensity of the blobs. The first operation can be achieved perfectly, whereas the second results in damping of coherence. This directionality imposed by the second law implies that coherence transfers, similarly to heat transfers, are generally irreversible.

5.4.2 Coherence merging under Thermal Operations

Let us now analyse a second primitive operation, coherence merging. Assume we are given a state ρ with two non-vanishing coherence terms in mode ω_0 : $|\rho_{10}| = a$ and $|\rho_{21}| = b$, and we want to merge them into a single coherence term ρ'_{10} (the results for merging into ρ'_{21} are analogous). Our bound (5.16) for symmetric operations yields:

$$\begin{aligned} |\rho'_{10}| &\leq \sqrt{p_{1|1}p_{0|0}}a + \sqrt{p_{1|2}p_{0|1}}b \leq \sqrt{p_{1|1}}a + \sqrt{p_{0|1}}b \\ &\leq \sqrt{p_{1|1}}a + \sqrt{1 - p_{1|1}}b. \end{aligned}$$

One can easily prove that the above bound is maximized for $p_{1|1} = a^2/(a^2 + b^2)$, so ultimately

$$|\rho'_{10}| \leq \sqrt{a^2 + b^2}. \quad (5.39)$$

We note that a symmetric merging map achieving the above bound can actually be constructed. Consider the following Kraus operator decomposition of a CPTP map:

$$M_j = \frac{1}{\sqrt{3}} \left[|0\rangle \left(e^{i\frac{2\pi j}{3}} \langle 0| + x \langle 1| \right) \right] + |1\rangle \left(e^{i\frac{2\pi j}{3}} \sqrt{1-x^2} \langle 1| + \langle 2| \right), \quad (5.40)$$

with $x \in [0, 1]$ and $j = \{0, 1, 2\}$. A direct calculation shows that this map is time-translation symmetric, by checking that each mode is mapped into itself.² In fact,

$$\sum_j M_j \rho M_j^\dagger = \frac{1}{3} [\rho_{00} + x^2 \rho_{11}] |0\rangle\langle 0| + \frac{1}{3} [\sqrt{1-x^2} \rho_{01} + x \rho_{12}] |0\rangle\langle 1| + h.c. + \frac{1}{3} [(1-x^2) \rho_{11} + \rho_{22}] |1\rangle\langle 1|.$$

²To see that this condition is sufficient for covariance of the channel, notice that, since $\mathcal{E}(\rho^{(\omega)})$ is in mode ω ,

$$\mathcal{U}_t^\dagger \circ \mathcal{E} \circ \mathcal{U}_t(\rho) = \sum_\omega e^{-i\hbar\omega t} \mathcal{U}_t^\dagger [\mathcal{E}(\rho^{(\omega)})] = \sum_\omega e^{-i\hbar\omega t} e^{i\hbar\omega t} [\mathcal{E}(\rho^{(\omega)})] = \sum_\omega \mathcal{E}(\rho^{(\omega)}) = \mathcal{E}(\rho) \quad \forall t.$$

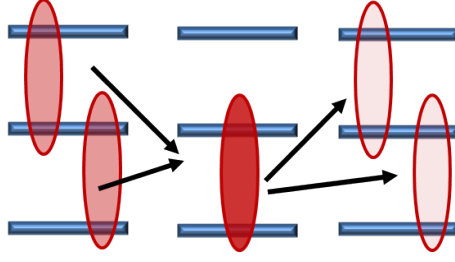


Figure 5.8. Irreversibility of coherence merging cycle. Merging of coherence elements that are “sharing an energy level” always results in irreversible losses, even if we merge into the lower energy term. The second law, however, imposes additional irreversibility that exponentially damps the contribution to high energy coherence coming from low energy coherence.

By direct calculation we can now show that

$$\begin{aligned} |\rho'_{10}| &= \left| \langle 1 | \left(\sum_{j=0}^2 M_j (a |1\rangle\langle 0| + b |2\rangle\langle 1|) M_j^\dagger \right) | 0 \rangle \right| \\ &= \sqrt{1 - x^2} a + x b. \end{aligned}$$

The choice $x = b/\sqrt{a^2 + b^2}$ saturates the bound (5.39).

It is also interesting to note that coherence merging at the maximum rate $a + b$ cannot be achieved (see Fig. 5.8), as inevitable losses arise when the two coherence terms have an overlap, i.e., both correspond to the coherence between state $|1\rangle$ and one of the other two states. This property distinguishes merging from shifting.

Let us now switch to the thermodynamic scenario. The bound for merging two coherences into a single coherence term now depends on whether one merges into high energy coherence or into low energy coherence. By applying a similar reasoning as in the case of symmetric operations we obtain bounds for coherence merging under Thermal Operations. In fact, the bound on $|\rho'_{10}|$ can be found in the same way as in the covariant case, whereas for the bound on $|\rho'_{21}|$ we can use

$$\begin{aligned} |\rho'_{21}| &\leq \sqrt{p_{2|1} p_{1|0}} a + \sqrt{p_{1|1} p_{2|2}} b \leq \sqrt{e^{-\beta \hbar \omega_0} p_{1|0}} a + \sqrt{p_{1|1}} b \\ &\leq \sqrt{e^{-\beta \hbar \omega_0} (1 - p_{1|1})} a + \sqrt{p_{1|1}} b. \end{aligned}$$

A simple optimisation gives $p_{1|1} = b^2/(a^2 + b^2)$, that leads to the following bounds (it is unclear if these are tight):

$$|\rho'_{10}| \leq \sqrt{a^2 + b^2}, \quad \text{for merging down,} \quad (5.41a)$$

$$|\rho'_{21}| \leq \sqrt{e^{-\beta \hbar \omega_0} a^2 + b^2}, \quad \text{for merging up.} \quad (5.41b)$$

Finally, let us note that the qutrit example does not exhaust all the merging scenarios. One of the reasons is that the non-trivial mode in the case analyzed is composed

of two off-diagonal elements that are overlapping. For higher dimensional systems one can imagine a situation in which elements of the same mode are not overlapping, e.g., $|1\rangle\langle 0|$ and $|3\rangle\langle 2|$ for a system with equidistant spectrum. In contrast to the overlapping case for symmetric operations one can then perform perfect merging using the shift operation from the previous section, see Eqs. (5.36a) and (5.36b). However, we leave the comprehensive study of the set of building blocks for manipulating coherence for future research.

5.5 Conclusions

In this chapter we aimed at several things. The broad approach was to analyse coherence manipulations in thermodynamics from a symmetry-based perspective. Specifically, the underlying energy-conservation within thermodynamics was shown to constrain all thermodynamic evolutions to be “symmetric” under time-translations in a precise sense. This, in turn, allowed us to make use of harmonic analysis techniques, developed in [42], to track the evolution of coherence under thermodynamic transformations in terms of the “mode components” of the system. This constitutes a natural framework to understand coherence, thus allowing us to separate out the constraints that stem solely from symmetry arguments from those particular to thermodynamics, and provides results that generalize recent work on coherence [86]. This approach also implies that the existing single-shot results applicable to block-diagonal results, constrained by thermo-majorization, can be viewed as particular cases of our analysis when only the zero-mode is present. Beyond this regime we have shown that every non-zero mode obeys *independent* constraints and displays thermodynamic irreversibility similar to the zero-mode.

Exploiting these tools we arrived at inequalities linking initial and final coherences in the energy eigenbasis. We have shown that a rich dynamics is allowed, in which coherence can be transferred among different energy levels within each mode, and that, similarly to heat flows, coherence flows show directionality due to the limitations imposed by the second law. Finally, we have also presented a way to find the guaranteed amount of coherence that can always be preserved under thermodynamic transformations.

The extraction of work from the coherence of a quantum state would require the transfer of free energy “living” in modes $\omega \neq 0$ into the zero mode of a battery system. It should be clear from the mode picture that this is impossible by means of Thermal Operations. However, transfer of coherence between two different modes can be mediated by an auxiliary system carrying coherence or, to say it in the language used in Chapter 4, by a quantum reference frame. This is what we will explore in the next chapter.

Remark 5.13 (Open question). Eq. (2.22) gives conditions equivalent to thermo-majorisation, guaranteeing the existence of a Gibbs-preserving stochastic map between two probability distributions. Alberti-Uhlmann’s theorem gives a quantum analogue for qubit systems [90]. Can we transform it into a simpler statement about a suitably defined set of (necessary) “quantum-thermo-majorisation” conditions? Intuitive arguments and the qubit

case suggest to look at the weak majorisation condition $\gamma_S^{-1/2} \rho \gamma_S^{-1/2} \succ_w \gamma_S^{-1/2} \sigma \gamma_S^{-1/2}$ (“weak” here stands for the fact that the $k = n$ equality condition is dropped from the definition of majorisation). Is this weak majorisation condition equivalent to the conditions of Alberti-Uhlmann’s theorem? If so, what can we learn from them beyond the qubit case?

6 The extraction of work from quantum coherence

The interplay between quantum-mechanical properties, such as coherence, and classical notions, such as energy, is a subtle topic at the forefront of quantum thermodynamics. The traditional Carnot argument limits the conversion of heat to work; here we critically assess the problem of converting coherence to work. Through a careful account of all resources involved in the thermodynamic transformations within a fully quantum-mechanical treatment, we show that there exist thermal machines extracting work from coherence arbitrarily well. Such machines only need to act on individual copies of a state and can be reused. On the other hand, we show that for any thermal machine with finite resources not all the coherence of a state can be extracted as work. However, even bounded thermal machines can be reused infinitely many times in the process of work extraction from coherence.

6.1 Introduction

Scientia potentia est, knowledge is power, the latin aphorism goes. This could not be more true in thermodynamics, where knowledge about the state of a system can be exploited to our advantage to extract work from it [92, 93]. In quantum mechanics states of maximal knowledge are called pure states. A peculiar feature of the quantum world is that, due to the superposition principle, even for such states there are many questions that cannot be answered sharply. In thermodynamics we are especially interested in energetic considerations and so an odd place is taken by pure states that are a superposition of different energy states. This is because, despite the fact that we possess full knowledge about the system, our possibility of predicting the outcome of an energy measurement can be very limited.

In standard quantum-mechanical considerations this is not a issue, because we can always reversibly transform a pure state into any other pure state by unitary dynamics. A basic task of thermodynamics, though, is the book-keeping of all energy flows from and out of the system, and there is no reversible transformation mapping a superposition of different energy states into an eigenstate while strictly conserving energy. Hence, we are left to wonder whether the “scientia” of having a pure state with quantum coherence can be converted into “potentia” of extracted work, while being limited by the law of energy conservation.

More precisely, we analyze work extraction from quantum coherence.¹ We first set the scene by presenting existing approaches to the problem of work extraction from the coherence of quantum systems. We argue that, within the regime of individually processed systems, the current approaches fail to account for all the resources used during the work extraction protocol. The typical assumption is to use a classical external field that experiences no back-reaction [74, 94]. However, this does not allow for a full accounting of the thermodynamic cost of maintaining the field. Although this cost may be small in a single use, it has to be accounted for since the work gain will also be small. Hence we propose an alternative framework that aims for a careful book-keeping of resources.

In particular, we use the notion of a *thermal machine* [95], a device of bounded resources that can be used to manipulate thermodynamical systems and perform tasks such as work extraction. Our thermal machine incorporates the use of an ancillary system carrying coherence (henceforth called *reference system*), introduced into the context of coherence manipulation in thermodynamics in [33]. It also includes a battery system where work can be stored, or transferred to the reference when necessary. A crucial question addressed in this work will be how to use the thermal machine in a repeatable way, i.e. without deteriorating it. We make use of an important result of Johan Åberg, showing that reference systems can be used repeatedly to manipulate coherence [34]. However the reference needs to be repumped for the machine to continue to operate. The work cost of repumping needs to be taken into account, which can mean that the thermal machine will not be able to extract all the available work from coherence. Nonetheless, we will find that we can come arbitrarily close, by choosing the amount of coherence resources carried by the reference system in the machine appropriately large.

On the other hand, for any given thermal machine, we will prove that one can never extract all the available work. We will show that coherences of individual quantum systems can be exploited to enhance the performance of work extraction protocols (both in the average and the single-shot sense), but not to the extent that could be expected in the “classical” limit. Moreover, the work extraction protocol we provide does not deteriorate the thermal machine.

6.2 Coherence and work

6.2.1 Setting the scene

Let us start by introducing the framework that we will use throughout this chapter and collect the core assumptions that our results rest upon. We want to study the allowed thermodynamic transformations by explicitly modelling any coherence resources being used. As we shall see, the assumption that no coherence or work resources are used without accounting will naturally lead us to the set of Thermal Operations. This con-

¹Here, and in the rest of this chapter, we use the term “coherence” in the sense of “superposition of states belonging to different energy eigenspaces”.

nects to the framework of the previous chapters, characterised by work-locking. To go beyond work-locking we will allow for non-thermal ancillary systems to be used, i.e. a reference frame as well as a battery to store work. However, care must be taken so that we book-keep every resource that is being consumed in the process (this is paramount in small-scale thermodynamics). This means these ancillae are explicitly included in the formalism as quantum systems and their evolution is analysed. This will lead to a spectrum of possibilities, in which the properties of the auxiliary systems tell us how close we can get to a classical limit in which all work can be extracted from coherence. This may remind the reader of the classical limit analysed in the second part of Sec. 4.3.1; however, in stark difference from there, we will not allow operations on more than a system at a time. A classical limit will nevertheless emerge, not by collective actions on a large number of systems, but by operating with an effectively classical field on single quantum systems.

Let us now describe in detail the assumptions made. There are two ways in which coherence can enter the thermodynamics of the systems under consideration. This can happen either explicitly, by transferring it from an external system with quantum coherence (a trivial example being a swap operation between the system and an ancillary coherent state); or implicitly, by allowing operations that do not conserve energy (e.g., $|0\rangle \rightarrow |+\rangle$, where the Hamiltonian is given by $H_S = |1\rangle\langle 1|$) or conserve it only on average (e.g., $|1\rangle \rightarrow (|0\rangle + |2\rangle)/\sqrt{2}$, with $H_S = |1\rangle\langle 1| + 2|2\rangle\langle 2|$). Therefore, we will only allow for those transformations that do not implicitly introduce coherence:

Assumption 1 (Allowed transformations). The set of allowed transformations is given by all (strictly) energy-preserving unitaries, i.e., unitaries that commute with the total free Hamiltonian of the system. The use of all ancillary systems should be *explicitly* accounted for.²

We will also take a closer look at an alternative approach in Sec. 6.2.4 and explain why we find it not satisfactory for the aims of the present work.

In this chapter we focus on the task of work extraction from quantum systems with coherence. We do not aim here to settle the long-standing issue of what is an appropriate definition of work in quantum thermodynamics (see, e.g., [37, 96]). For the scope of this work we will assume, for the sake of simplicity, that the following holds for classical (incoherent) states:

Assumption 2 (Average work, incoherent states). Let ρ_S be a quantum state of the system described by Hamiltonian H_S , with ρ_S being incoherent in the energy eigenbasis. Then, in the presence of a heat bath at temperature T , an average amount of work $\langle W \rangle(\rho_S)$ equal to the change of free energy of a state can be extracted from it:

$$\langle W \rangle(\rho_S) = \Delta F(\rho_S) := F(\rho_S) - F(\gamma_S), \quad (6.1)$$

where $F(\sigma) := \text{Tr}[\sigma H_S] - kTS(\sigma)$, $S(\cdot)$ is the von Neumann entropy and $\gamma_S = e^{-H_S/kT}/Z_S$

²As we will see, thermal ancillae are the only ones that can be freely introduced without trivialising the problem of work extraction.

is a thermal state with Z_S being the partition function of the system.

This formula, consistent with traditional thermodynamics, has been obtained using work extraction models that differ in details, but agree on the result [46, 74]. In this thesis, it was proven for qubit systems in the box of Section 3.1.2. For example, in Ref. [46] the work extraction protocol is based on two elementary processes: level transformations (that change the eigenvalues of the system Hamiltonian H_S) and full thermalisation with respect to the current system Hamiltonian (through thermal contact with a bath at temperature T). Average work is then defined as the average change in energy during level transformations (the “unitary” steps) and, if initial and final Hamiltonian coincide, Eq. (6.1) is recovered. Here we focus on the problem of extending Eq. (6.1) to quantum states with coherence. What follows applies to any definition of work satisfying Assumption 2.

The problem of work extraction can also be studied in the so-called single-shot regime. This means that one is interested in single instances of the work extraction protocol, instead of average quantities. To explain this more precisely, let us refer again to the model introduced in Ref. [46] that we have summarised above. Extracted work can then be seen as a random variable, maximising the average of which yields Eq. (6.1). However, we may instead ask what is the maximum amount of deterministic (i.e., fluctuation-free) work that can be extracted during a single instance of the protocol, while allowing the failure probability ϵ . In Ref. [46] it was shown that for incoherent states this quantity is given by $F_0^\epsilon(\rho_S) - F(\gamma_S)$, where $F_0^\epsilon(\rho_S) = -kT \log Z_\epsilon$ is a single-shot free energy defined as follows. Given a subset Λ of the indices $\{i\}$ labelling the energy levels of the system, define $Z(\Lambda) = \sum_{i \in \Lambda} e^{-\beta E_i}$, where E_i are the eigenvalues of H_S , associated to eigenstates $|E_i\rangle$. Then $Z_\epsilon = \min\{Z(\Lambda) : \sum_{i \in \Lambda} p_i > 1 - \epsilon\}$, where $p_i = \langle E_i | \rho_S | E_i \rangle$. This result is also in agreement with other work extraction models based on Thermal Operations [24]. Hence, for the single-shot scenario we can use the following assumption:

Assumption 3 (Single-shot work, incoherent states). Let ρ_S be a quantum state of the system described by Hamiltonian H_S , with ρ_S being incoherent in the energy eigenbasis. Then in the presence of a heat bath at temperature T , using a single-shot protocol one can extract a sharp amount of work W_{ss}^ϵ with failure probability ϵ :

$$W_{ss}^\epsilon(\rho_S) = \Delta F_0^\epsilon(\rho_S) := F_0^\epsilon(\rho_S) - F(\gamma_S). \quad (6.2)$$

Once again, our aim is to extend Eq. (6.2) to quantum states with coherence and our results apply to any definition of single-shot work satisfying Assumption 3. For the sake of brevity in the remaining of this work we will only write “extracting work equal to the free energy”, omitting “in the presence of a heat bath at temperature T ”; however, this is how our claims should be understood.

In thermodynamic considerations thermal Gibbs states are the only ancillary states that can be introduced without the need for careful accounting. In fact, one can show that using energy-preserving unitaries (in accordance with Assumption 1), a thermal state is the only one that can be introduced for free without allowing the production of every

other incoherent state [23]. Clearly, if this was possible, then from Assumptions 2 and 3 one could extract infinite amount of work, thus trivialising the theory. Hence, the most general thermodynamic transformations that can be performed without using extra resources are given by:

1. adding a bath system in a thermal state γ_E with arbitrary Hamiltonian H_E and fixed temperature T ,

$$\rho_S \mapsto \rho_S \otimes \gamma_E, \quad \gamma_E = e^{-\beta H_E} / \text{Tr} [e^{-\beta H_E}], \quad \beta = 1/kT; \quad (6.3)$$

2. performing any global unitary that conserves total energy, i.e., that commutes with the total free Hamiltonian of the system and baths, in accordance with Assumption 1;
3. discarding any subsystem.

The set of quantum maps acting on a system that arise from combining the transformations described above is the set of Thermal Operations (see Sec. 2.2.2)

6.2.2 Work-locking

The aim is to begin with a system initially in a state with coherence ρ_S , and finish with a thermal state γ_S , while optimally increasing the free energy of a battery (storage) system. The initial and final battery states, ρ_B and ρ'_B , should be incoherent, so that using Assumptions 2 and 3 we can achieve the coherence to work conversion that we are looking for. Schematically:

$$\rho_S \otimes \rho_B \rightarrow \gamma_S \otimes \rho'_B. \quad (6.4)$$

Without the use of an ancillary resource state the above transformation is given by a Thermal Operation. Hence, the phenomenon of work-locking described in Sec. 4.3 becomes crucial. Recall that Thermal Operations commute with the dephasing channel D (introduced in Def. 3.2).³ Hence, we get that if the transformation described by Eq. (6.4) is possible, also the following one is: $D(\rho_S) \otimes \rho_B \rightarrow \gamma_S \otimes \rho'_B$. This implies $\Delta F(\rho_B) \leq \Delta F(D(\rho_S))$, because F is non-increasing under thermal operations. From Assumption 2 we then have $\langle W \rangle(\rho_S) \leq \langle W \rangle(D(\rho_S))$. A similar argument gives also $W_{ss}^e(\rho_S) \leq W_{ss}^e(D(\rho_S))$; note that in both cases the bound is achievable because dephasing is a Thermal Operation. This phenomenon, called “work-locking” in Chapter 4, highlights that despite contributing to the free energy of the state, quantum coherence does not contribute to work extraction: it is “locked”. It also shows, as discussed in Chapter 4, that the standard formula $\langle W \rangle(\rho_S) = \Delta F(\rho_S)$ applied to every state (also the ones with coherence), implicitly assumes the access to an external source of coherence. In this chapter we revise the

³For simplicity we omit the subscript indicating the Hamiltonian with respect to which dephasing is performed.

problem of extracting work from coherence, clarifying the role of this external source of coherence. To summarise

Central Question. To what extent can Eq. (6.1) and Eq. (6.2) be extended to arbitrary quantum states with coherence, while explicitly accounting for coherence resources (ancillary systems)?

6.2.3 Different thermodynamic regimes

With an increasing interest in the thermodynamics of non-equilibrium quantum systems, an important distinction to make is between “single-shot” statements, which are valid for every run of the protocol, and “many-runs” statements, valid in the case of a large number M of runs. In the *asymptotic regime* $M \rightarrow \infty$ one is focused on studying average quantities (like average extracted work), which is justified by the fact that the fluctuations around the average can be made negligible in the limit of a large number of runs of the protocol (which is often the situation of interest in the study of heat engines). On the other hand, although the expected amount of extracted work can be studied in a single-shot regime [74], it potentially carries little information about the system at hand due to the large fluctuations of non-equilibrium thermodynamics [46]. Instead, the focus in the single-shot regime is typically on probabilistic work extraction protocols that guarantee precise and sharp amount of work with a finite probability of success or some minimum amount of guaranteed work [24, 46, 54, 97]. On top of this classification we can also differentiate between “individual processing” scenarios, in which a single (possibly microscopic) system undergoes a thermodynamic process on its own; and “collective” scenarios, in which $N > 1$ copies of a state are processed together (the $N \rightarrow \infty$ limit is considered in [33]). This classification of the thermodynamic regimes in which work extraction can be analysed is presented in Fig. 6.1.

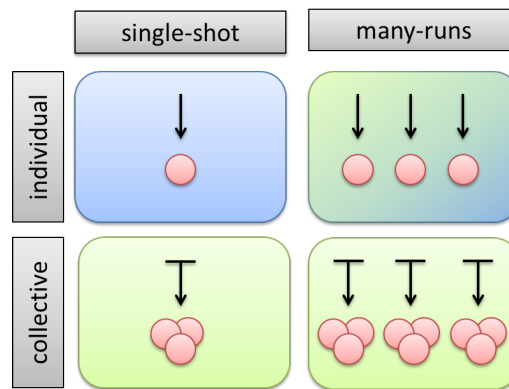


Figure 6.1. Thermodynamic regimes. Work extraction protocols can be investigated in different thermodynamic regimes. These can be classified by the number of systems that are processed at each run of the protocol (individual vs collective) and the number of times the protocol is repeated (single-shot vs many-runs). The green background indicates that in a given regime the maximal amount of work that can be extracted is consistent with traditional thermodynamics.

The work-locking described in the previous section is a feature appearing in the regime of individually processed quantum systems. On the other hand, allowing for collective processing of the systems or for an ancillary quantum memory, one can “unlock” work from quantum coherence (see box below).

Collective processing regime and quantum memories

In the collective processing regime work can be effectively unlocked from coherence. This is achieved by processing many copies of a system state ρ_S collectively and extracting work from relational degrees of freedom that live in the so-called decoherence-free subspaces [5, 33, 38, 81]. The intuitive explanation is that one copy of a state ρ_S with coherence can act as a reference for the other one, and we have $D(\rho_S^{\otimes 2}) \neq D(\rho_S)^{\otimes 2}$. In the case of finite number of copies $\rho_S^{\otimes N}$ a non-zero amount of work is unlocked from the coherences, and in the limit of processing collectively infinitely many independent and identically distributed (i.i.d.) copies, the amount of work per copy that can be extracted deterministically equals $F(\rho_S) - F(\gamma_S)$ (see Sec. 4.3).

Instead of collectively processing many copies of a system, one may also consider a black-box device B that takes in individual quantum systems ρ_S and at *each round* returns a thermalized state γ_S and an average amount of work equal to $F(\rho_S) - F(\gamma_S)$. From outside the box it seems we are dealing with a work extraction protocol that individually processes each state. However, the devious way in which the box achieves this is the following:

1. The box B contains a large quantum memory consisting of $N \gg 1$ copies of incoherent quantum states $\sigma_B^{\otimes N}$, for which $F(\sigma_B) = F(\rho_S)$.
2. Every time the box takes in a single copy ρ_S it swaps this state into memory and instead performs work extraction on one copy of σ_B . Hence it outputs on average $F(\rho_S) - F(\gamma_S)$ and a thermalised state γ_S .
3. After N uses its memory is filled with the coherent states $\rho_B^{\otimes N}$ and so it does large- N collective processing and restores to $\sigma_B^{\otimes N}$ with sublinear losses in N (see Sec. 4.3).

Although from the outside of the box this is identical to the individual processing regime, the collective, relational processing of coherence is “hidden” in the quantum memory.

As discussed in Sec. 4.3, in this limit coherence plays no role as, e.g., for N identical qubits $F(\rho^{\otimes N}) \approx F(D(\rho^{\otimes N}))$, with a deficit scaling as $\log N/N$ [5]. Hence, in this chapter we are interested in the thermodynamics of individual quantum systems ($N = 1$, the upper half of Fig. 6.1).

6.2.4 Individual processing regime

Average energy conservation

In [74] sharp energy conservation, as expressed by the unitary dynamics commuting with the total Hamiltonian H_{tot} , was replaced with the condition that such dynamics only keeps the first moment $\langle H_{\text{tot}} \rangle$ constant. Under this weaker condition it was shown that

an amount of energy equal to the free energy difference $\Delta F(\rho_S)$ can be extracted on average from a system in an arbitrary quantum state ρ_S .

The elegance and appeal of this is that it recovers a clear thermodynamic meaning for the free energy of an individual quantum system. However, several problematic issues can be raised. Firstly, if one is interested in analysing the class of allowed quantum operations, then in the average-energy scenario this set depends on the particular state one is processing, which is conceptually less appealing and technically problematic from a resource-theoretic perspective.

Secondly, restricting energy considerations to the first moment analysis can hide arbitrarily large energy fluctuations described by higher moments, that are not explicitly modeled, but may be highly relevant. To see this consider a unitary U_{av} mapping a state $|\psi_{02}\rangle := (|0\rangle + |2\rangle)/\sqrt{2}$ to $|1\rangle$, which preserves energy on average (here $|n\rangle$ is the energy eigenstate corresponding to energy n). Since microscopically all processes are ultimately energy-conserving, U_{av} must be realized through a joint energy-preserving unitary U involving $|\psi_{02}\rangle$ and some ancillary state ρ_A , e.g., the state of the battery,

$$U(|\psi_{02}\rangle\langle\psi_{02}| \otimes \rho_A)U^\dagger = |1\rangle\langle 1| \otimes \rho'_A.$$

In any such process the energy fluctuations of the ancillary system must increase. Specifically, denoting by H the Shannon entropy of the outcomes of an energy measurement one gets a strict inequality: $H(\rho'_A) > H(\rho_A)$. As an example, consider the ancillary system prepared in the energy eigenstate $|m\rangle$, so that an energy measurement would give a sharp outcome. Then, while the system is transformed from $|\psi_{02}\rangle$ into $|1\rangle$, the ancilla must be transformed into a superposition of energy eigenstates $(|m+1\rangle + |m-1\rangle)/\sqrt{2}$. Hence an energy measurement would show fluctuations in the final state of the ancilla.

A typical example is when $V = U_{\text{av}}$ is a unitary on a system plus a battery that conserves energy on average and is used to extract work from the system (see, e.g., [74]). The result above says that such process necessarily creates extra fluctuations in an ancilla, however these are not explicitly modelled within the formalism used. As we will see it is exactly due to these fluctuations that our protocols require work to be invested in restoring the ancillary state.

Consider a joint energy-conserving unitary U , i.e., $[U, H_S + H_A] = 0$, inducing the following evolution⁴

$$U(\rho_S \otimes \rho_A)U^\dagger = \rho'_S \otimes \rho'_A,$$

so that the final state of the system ρ'_S has no coherence in energy eigenbasis and $\rho'_S = V\rho_S V^\dagger$ for some unitary V (V may conserve energy on average, but cannot conserve energy strictly). The uncertainty of an energy measurement on ρ_A can be decomposed as [72]:

$$H(\rho'_A) = S(\rho'_A) + A(\rho'_A), \tag{6.5}$$

⁴We assume here the final state of the ancilla is uncorrelated from the rest. It may be interesting to investigate what happens when this is not the case.

where $A(\sigma) = S(\sigma||D(\sigma))$ is the relative entropy between a state and its decohered version and H is the Shannon entropy of the probability distribution of an energy measurement (the proof is essentially a re-writing of Eq. (4.18)). Because U commutes with the total Hamiltonian we have

$$A(\rho_S \otimes \rho_A) = A(\rho'_S \otimes \rho'_A).$$

As the final state of the system ρ'_S has no coherence we have $A(\rho'_S \otimes \rho'_A) = A(\rho'_A)$. Using $A(\rho_S \otimes \rho_A) > A(\rho_A)$, one gets that $A(\rho'_A) > A(\rho_A)$. From the invariance of the von Neumann entropy under unitary transformations, $S(\rho'_A) = S(\rho_A)$. So we conclude from Eq. (6.5)

$$H(\rho'_A) > S(\rho_A) + A(\rho_A) = H(\rho_A),$$

as anticipated.

As the fluctuations created by operations that conserve energy only on average remain outside the formalism, one cannot properly account for the fluctuations in the extracted work outside the asymptotic regime.

Repeatable use of coherence resources

As already mentioned in Sec. 6.2.2, in the presence of energy conservation and without additional coherence resources, work-locking prevents us from extracting work from the coherence of individual quantum systems. One could then stay within the framework of strict energy conservation, but allow for the use of an extra source of coherence. We refer to this extra system as the *reference* (see Sec. 4.3.2).

At one extreme one could allow for the use of an infinite source of coherence (an “unbounded” reference frame [38, 98]),⁵ that entirely negates the constraints and experiences no back-reaction from its use on the quantum system. In such case we should be able to extract all the work from coherence. However, one might worry that this involves the accounting “ $\infty - c = \infty$ ”, with c being some finite resource consumed from an infinitely large reference system. Indeed, the use of such an unbounded reference allows us to simulate the operations from the previous section (conserving energy only on average) [38], and hide the arising extra fluctuations in the infinitely large reference system. This semi-classical treatment is typical for many standard approaches that assume the existence of a classical field experiencing no back-reaction from the system [74, 94] and works well in many circumstances.⁶ However we are interested in the regime in which the thermal machine itself may be a microscopic quantum system. Hence, it seems more reasonable to firstly consider the reference as a quantum system with finite coherence resources – a “bounded” reference frame – and only then study in what precise sense the limit of an unbounded reference is approached (recent works in this spirit and the discussion of

⁵Not to be confused with a reference described by Hamiltonian unbounded from below, which is unphysical.

⁶Nevertheless, as discussed before, this still requires a careful analysis, because even if the deterioration of the field is small, the work extracted is small as well.

semiclassical approaches can be found, e.g., in [35–37]).

Definition 6.1 (Reference). We consider a reference (or coherence reservoir) given by an infinite-dimensional ladder system described by Hamiltonian $H_R = \sum_{n=0}^{\infty} n |n\rangle\langle n|$. We characterise the state ρ_R of the reference through two numbers, $(\langle\bar{\Delta}\rangle, M)$. The first parameter, $\langle\bar{\Delta}\rangle$, measures the coherence properties of the reference and is given by

$$\langle\bar{\Delta}\rangle = \text{Tr} [\rho_R \bar{\Delta}], \quad \bar{\Delta} = (\Delta + \Delta^\dagger)/2, \quad (6.6)$$

where Δ is the shift operator $\Delta = \sum_{n=0}^{\infty} |n+1\rangle\langle n|$. We have that $\langle\bar{\Delta}\rangle < 1$ and the limit case $\langle\bar{\Delta}\rangle = 1$ is called *unbounded* or classical reference. The second parameter, M , describes the lowest occupied energy state, $M = \min\{n : \langle n | \rho_R | n \rangle > 0\}$.

Examples of a sequence of references that come arbitrarily close to a classical one are uniform superpositions of L energy states when $L \rightarrow \infty$ or coherent states with arbitrarily large amplitude. The use of $\langle\bar{\Delta}\rangle$ and M as relevant quality parameters will soon become clear.

Results from the field of quantum reference frames [38, 98–101] suggest that the back-reaction experienced by the reference will deteriorate it and consume the resources. However, if the usefulness of the reference or field is continually degraded during the work extraction process, we cannot claim that we are presenting a protocol performing work extraction from the state alone, as extra resources are consumed. Similar problems arise if free energy is continually taken away from the reference.

Here we propose the following approach. We allow for the use of additional coherence resources as part of our thermal machine, but demand that they are used *repeatably* in the following sense: the performance of our reference-assisted protocol, while operating individually on the n -th copy of the system, must be the same as while operating on the $(n+1)$ -th copy, for all $n \in \mathbb{N}$. In other words, repeatability means that the reference’s ability to perform the protocol never degrades, but crucially its state is allowed to change. Essentially this means that despite that the free energy of the reference can fluctuate and its coherence properties change, it can be used indefinitely to repeat the same protocol. To design such a protocol we employ the recent surprising result of [34] that shows how a coherence resource can be used repeatably to lift the symmetry constraints imposed by energy conservation.⁷ However, as we will see, the protocol in [34] requires continuous injection of energy into the reference (we do not allow the Hamiltonian of the reference to be unbounded from below, as in [102]). Hence, it is not immediately obvious that net thermodynamic work can be extracted from coherence.

In what follows we introduce a general protocol that processes quantum systems individually and allow us to extract work from their coherence. We then focus on two

⁷The work [34] actually uses the word “catalysis”, but we prefer to use the word repeatability/repeatable to avoid suggesting that there is no change in the state of the reference. Recall that traditionally a catalyst is a system in a state χ that enables $\rho \otimes \chi \rightarrow \sigma \otimes \chi$, despite $\rho \rightarrow \sigma$ being impossible (see Section 2.1.5 and, e.g., [23, 30]). Repeatability, on the other hand, only requires the auxiliary system to be as useful at the end as it was at the beginning, while its state may change.

	Single-shot	Asymptotic
Average energy conservation	$\langle W \rangle = \Delta F$ [74] Large fluctuations [46]	$\langle W \rangle = \Delta F$ [74]
Strict energy conservation	$\epsilon(\gamma\rangle) = \epsilon(\gamma_S), \langle W \rangle = 0$ [5, 24, 81]	
Strict energy conservation with resource used repeatably	$\epsilon(\gamma\rangle) = 0$ for unbounded reference $\epsilon(\gamma\rangle) < \epsilon(\gamma_S)$ for bounded reference	$\langle W \rangle = \Delta F$ for unbounded reference $\langle W \rangle < \Delta F$ for bounded reference

Table 6.1. Individual processing protocols extracting work from $|\gamma\rangle$. $\langle W \rangle$ denotes the average work that can be extracted from the coherent thermal state $|\gamma\rangle$ and ϵ denotes the error probability of a single-shot work extraction from a given state. A thermal state of the system is denoted by γ_S . Note that under operations strictly conserving energy, no work extraction protocol on $|\gamma\rangle$ can outperform a work extraction protocol on γ_S , as the two states are indistinguishable (see Sec. 4.3.1 and 4.3.2).

variations of it. The first one can come arbitrarily close to extracting all the coherence as average work with arbitrarily small failure probability, provided we make the coherence resources of the reference system in the thermal machine large enough. However, if one does not have access to arbitrarily large coherence resources, this variation of the protocol does not guarantee perfect repeatability. Therefore, we examine a second variation that is perfectly repeatable even for bounded references. We show then that the performance of work extraction in both the single-shot and asymptotic regimes is enhanced only if the quality of the reference (defined further in the text) is above a certain threshold.

6.3 The protocol

We analyze work extraction from pure qubit states with coherence,

$$|\psi\rangle = \sqrt{1-p}|0\rangle + \sqrt{p}e^{-i\varphi}|1\rangle, \quad p \in (0, 1). \quad (6.7)$$

Without loss of generality we can set $H_S = |1\rangle\langle 1|$ and $\varphi = 0$ (rotations about the Z axis of the Bloch sphere conserve energy). Our aim is to unlock work from coherence through the repeatable use of a thermal machine containing a reference, while processing each copy of $|\psi\rangle$ individually. In Table 6.1 the results we obtain within this framework are schematically compared with the ones obtained within the frameworks presented in the previous section for the paradigmatic example of a qubit in a “coherent Gibbs state” $|\gamma\rangle$ given by:

$$|\gamma\rangle = \sqrt{1-r}|0\rangle + \sqrt{r}|1\rangle, \quad (6.8)$$

with $(1-r, r)$ being the thermal distribution for the system, so that $D(|\gamma\rangle\langle\gamma|) = \gamma_S$ (so, $g = 1-r$).

The extraction of non-zero work from $|\psi\rangle$ then requires a thermal machine containing a reference state ρ_R and implementing an energy-conserving unitary V :

$$\rho'_{SR} = V(|\psi\rangle\langle\psi| \otimes \rho_R)V^\dagger,$$

satisfying the following:

1. The system is pre-processed to a new state $\rho'_S = \text{Tr}_R[\rho'_{SR}]$ that allows for better work extraction than from the initial state $|\psi\rangle$.
2. The final reference state $\rho'_R = \text{Tr}_S[\rho'_{SR}]$ can be processed into a state ρ''_R (perhaps using some of the extracted work) in such a way that the repeatability requirement is satisfied.
3. No collective operations, at any stage of the protocol, are allowed on multiple copies of $|\psi\rangle$ and no quantum memory (in the sense described before) is used.

6.3.1 The explicit work-extraction protocol

A protocol satisfying the above requirements consists of the following steps (see Fig. 6.2):

1. **Pre-processing.** The system $|\psi\rangle$ interacts through an energy-preserving unitary $V(U)$ with the reference ρ_R . The unitary acting on the joint system SR is chosen as in [34] to be:

$$V(U) = |0\rangle\langle 0| \otimes |0\rangle\langle 0| + \sum_{l=1}^{\infty} V_l(U), \quad (6.9)$$

with

$$V_l(U) = \sum_{n,m=0}^1 \langle n|U|m\rangle |n\rangle\langle m| \otimes |l-n\rangle\langle l-m|.$$

We choose

$$U = \begin{pmatrix} \sqrt{p} & -\sqrt{1-p} \\ \sqrt{1-p} & \sqrt{p} \end{pmatrix},$$

so that U rotates the qubit system from $|\psi\rangle$ to $|1\rangle$.⁷

2. **Work extraction.** The system is now in a state ρ'_S and, due to work-locking (see Sec. 6.2.2), is indistinguishable from its dephased version in any work extraction protocol. So without loss of generality we can use the dephased version

$$D(\rho'_S) = (1-q)|0\rangle\langle 0| + q|1\rangle\langle 1|. \quad (6.10)$$

⁷The interaction $V(U)$ corresponds to a modified Jaynes-Cummings model (with excitation-dependent coupling strengths). However, it can also be approximately realized within the standard Jaynes-Cummings model using a reference in a coherent state $|\alpha\rangle$, with $|\alpha|$ large enough (for details see Supplementary Material Sec. V in [34]).

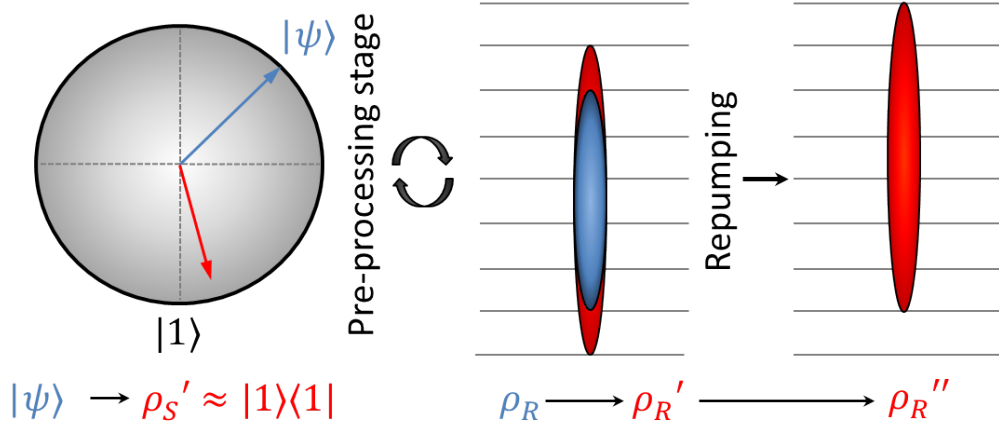


Figure 6.2. The basic protocol. The evolution of the system from the initial state $|\psi\rangle$ to the final state is depicted on the Bloch ball, in blue and red respectively. The evolution of the reference from the initial state (smaller blue blob) throughout the protocol (red blobs) is depicted on the energy level ladder.

Now, depending on the regime considered, single-shot or average (asymptotic) work can be extracted from the dephased state and stored in the thermal machine.

3. **Repumping.** The back-reaction changes the state of the reference into ρ_R' . Using part of the extracted work (stored in the battery during the previous step) we can repump the reference to shift it up:

$$\rho_R' \rightarrow \rho_R'' := \Delta \rho_R' \Delta^\dagger, \quad (6.11)$$

Δ is not a unitary, but note that this is actually not a problem. In fact, such operation can be realized through a joint energy-conserving unitary between the weight system in a state $|1\rangle$ and the reference in a state ρ_R' . The unitary is given by $V(U)$ in Eq. (6.9), where we take $U = X$, the Pauli X operator. Then

$$V(X) = \sigma_- \otimes \Delta + \sigma_+ \otimes \Delta^\dagger + |0\rangle\langle 0| \otimes |0\rangle\langle 0|,$$

where $\sigma_+ = |1\rangle\langle 0|$ and $\sigma_- = |0\rangle\langle 1|$. As the reference has no population in the ground state, the final state of the weight system is $|0\rangle$ and the final state of the reference is given by Eq. (6.11).

We will describe how often we perform the repumping while analysing different variations of the protocol.

4. We can repeat the protocol using ρ_R'' and a fresh copy of $|\psi\rangle$.

6.3.2 Performance

During the pre-processing stage the joint unitary $V(U)$ approximately induces U on the system:

$$\rho'_S \approx U(|\psi\rangle\langle\psi|)U^\dagger = |1\rangle\langle 1|.$$

The degree to which the above equation holds depends on the *quality* of the reference. In particular, the system final occupation in the excited state, $q = \langle 1|\rho'_S|1\rangle$, is given by

$$q = 1 - 2p(1-p)(1 - \langle \bar{\Delta} \rangle) - (1-p)^2 R_{00}, \quad (6.12)$$

where $R_{00} = \langle 0|\rho_R|0\rangle$ and $\bar{\Delta}$ is the quality parameter from Definition 6.1.

To see this it is useful to rewrite V in terms of Δ as follows:

$$V = (1 - \sqrt{p})|0\rangle\langle 0| \otimes |0\rangle\langle 0| + \sqrt{p}\mathbb{I} \otimes \mathbb{I} + \sqrt{1-p}(\sigma_+ \otimes \Delta^\dagger - \sigma_- \otimes \Delta) \quad (6.13)$$

Then one can compute $q = \langle 1|\text{Tr}_R[V(\rho_S \otimes \rho_R)V]|1\rangle$, getting

$$q = \langle 1| \left[(1-p)^2 |1\rangle\langle 1| \text{Tr}[\Delta^\dagger \rho_R \Delta] + p\rho_S + \sqrt{p(1-p)} (\rho_S |0\rangle\langle 1| \text{Tr}[\rho_R \Delta] + |1\rangle\langle 0| \rho_S \text{Tr}[\Delta^\dagger \rho_R]) \right] |1\rangle.$$

Using $\Delta\Delta^\dagger = \mathbb{I} - |0\rangle\langle 0|$ and the definition of $\bar{\Delta}$, simple manipulations lead to Eq. (6.12).

From Eq. (6.12) it is easy to see that $q \rightarrow 1$ when $R_{00} \rightarrow 0$ (i.e., when reference quality parameter $M > 0$) and $\langle \bar{\Delta} \rangle \rightarrow 1$. Therefore, R_{00} and $\langle \bar{\Delta} \rangle$ are operationally well-defined quality parameters of the reference, because they directly measure its ability to induce the unitary U that we want to perform on the qubit.

At the same time the reference undergoes a back-reaction induced by the joint unitary $V(U)$. This is described by the following Kraus operators:

$$A_0 = (1 - \sqrt{p})\sqrt{1-p}|0\rangle\langle 0| + \sqrt{p(1-p)}(\mathbb{I} - \Delta), \quad A_1 = p\mathbb{I} + (1-p)\Delta^\dagger. \quad (6.14)$$

These can be computed by looking at the action on a pure reference $|\psi_R\rangle$ (the definition is then extended by linearity to all mixed states):

$$V|\psi\rangle \otimes |\psi_R\rangle = [(1 - \sqrt{p})\sqrt{1-p}|0\rangle \otimes |0\rangle\langle 0| + \sqrt{p}|\psi\rangle \otimes \mathbb{I} + \sqrt{1-p}(\sqrt{1-p}|1\rangle \otimes \Delta^\dagger - \sqrt{p}|0\rangle \otimes \Delta)]|\psi_R\rangle$$

It is then simple to compute A_0 and A_1 by projecting this expression on the states $|0\rangle$ and $|1\rangle$ of the system.

Hence, the reference state after performing the pre-processing stage is given by:

$$\rho'_R = A_0 \rho_R A_0^\dagger + A_1 \rho_R A_1^\dagger. \quad (6.15)$$

From Eqs. (6.10) and (6.12) the only two parameters relevant for work extraction are the reference population in the ground-state, R_{00} , and the parameter $\langle \bar{\Delta} \rangle$. Using the Kraus operators specified by Eq. (6.14), the change in $\langle \bar{\Delta} \rangle$ during the pre-processing stage (i.e., the difference between the final and initial value of $\langle \bar{\Delta} \rangle$) can be computed and is found

to be:

$$\delta\langle\bar{\Delta}\rangle = (1-p)[(\sqrt{p}-1)\text{Re}(R_{01}) - \sqrt{p}R_{00}], \quad (6.16)$$

where as before $R_{ij} = \langle i|\rho_R|j\rangle$. A sufficient condition for $\langle\bar{\Delta}\rangle$ to stay constant is $R_{00} = 0$, i.e., $M > 0$. Therefore, if the initial state satisfies $R_{00} = 0$ exactly, performing the pre-processing stage does not change $\langle\bar{\Delta}\rangle$, as noted in [34]. We require step (3) of the protocol to ensure that $\langle 0|\rho_R''|0\rangle = 0$ (moreover, this step does not affect the coherence properties of the reference). If this is the case, at the end of the protocol we are left with the reference described by the same quality parameters R_{00} and $\langle\bar{\Delta}\rangle$ as at the beginning, and the reference ρ_R'' is as good as ρ_R within the protocol.

Finally, because the state of the reference changes, its free energy can fluctuate. However, notice firstly that the reference has Hamiltonian bounded from below, so for fixed average energy it has a finite amount of free energy. Secondly, repeatability requires that the reference can be used an arbitrary number of times and the performance of the protocol never changes. It is then easy to see that on average the free energy of the reference cannot be extracted as work, as this would be incompatible with repeatability. It can be shown that in the worst-case scenario the free energy change in the reference fluctuates around zero (see Aside 6.1).

Mathematical Aside 6.1. Free energy change in the reference

We show that the free energy change in the reference is, on average, bigger or equal than zero. Denote by $\Delta F_{R,n}$ the change in the free energy of the reference at the n -th repetition of the protocol. The total free energy change of the reference after M repetitions of the protocol satisfies $\sum_{n=1}^M \Delta F_{R,n} \geq F(\gamma_R) - F(\rho_R) \quad \forall M$, where γ_R is the thermal state of the reference. Hence, the average change in the free energy of the reference as $M \rightarrow \infty$ is

$$\overline{\Delta F_R} := \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{n=1}^M \Delta F_{R,n} \geq 0.$$

Moreover, these fluctuations vanish in the limit of an unbounded reference $\langle\bar{\Delta}\rangle \rightarrow 1$, as then the entropy of the reference stays constant, while its average energy is non-decreasing. We sketch here the argument. Notice that if $R_{00} = 0$,

$$\text{Tr} [A_0 \rho_R A_0^\dagger] = p(1-p)[(2 - 2\langle\bar{\Delta}\rangle)] \rightarrow 0, \text{ as } \langle\bar{\Delta}\rangle \rightarrow 1. \quad (6.17)$$

Then, only the action of A_1 matters. A_1 cannot decrease the energy of the reference. Moreover, noticing that $\text{Tr} [\bar{\Delta} \rho_R] < 1$ for every choice of ρ_R , we see that the $\langle\bar{\Delta}\rangle \rightarrow 1$ limit is an asymptotic limit in which the state of the reference approximates an eigenstate of Δ . In this limit A_1 approaches the identity on the reference, so the reference experiences no back-reaction.

6.4 Fundamental limitations of coherence to work conversion

How well does the above approach do in terms of work extraction? Here, we first emphasize the limitations on work extraction from coherence that arise due to the reference being bounded, i.e., when we have access to limited coherence resources. More precisely, we will explain why the use of a bounded reference does not allow one to extract from a state with coherence an average amount of work equal to the free energy difference.

However, we will then also show that one can construct a series of bounded reference states that come arbitrarily close to extract the free energy $\Delta F(|\psi\rangle)$, with protocols arbitrarily close to perfect repeatability.⁸ Thus, we will prove that in the limit of an unbounded reference all coherence can be converted into work in a repeatable way. The limit case does not generate any entropy in the reference system and, being a reversible transformation, is optimal.

6.4.1 Limitations of bounded thermal machines

In order to illustrate the limitations arising from using a bounded reference we will consider a particular model of work extraction from coherence described in Refs. [74, 94]. It has been proved there that the free energy difference $\Delta F(\rho_S)$ can be extracted from a system ρ_S as work if one allows for the use of operations that conserve energy only on average. Let us briefly recall the protocol used to achieve this. It is composed of two stages; first, given a state ρ_S , work is extracted from coherence (and partially from the population, as the occupation over energy changes). Second, work is extracted from an incoherent state.

Without loss of generality we can write any state ρ_S as $\sum_n p_n |\psi_n\rangle\langle\psi_n|$ with $p_{n+1} \leq p_n$. Let us also denote the Hamiltonian of the system by $H_S = \sum_n E_n |E_n\rangle\langle E_n|$. In the protocol that allows to extract work from coherence in Ref. [74], the system ρ_S interacts with a weight system in a gravitational field via the unitary

$$U_{av} = \sum_n |E_n\rangle\langle\psi_n| \otimes \Gamma_{\varepsilon_n}, \quad (6.18)$$

where Γ_{ε_n} is the shift operator on the weight system that shifts it in energy by $\varepsilon_n = \langle\psi_n| H_S |\psi_n\rangle - E_n$. The final state of the system is $\rho'_S = \sum_n p_n |E_n\rangle\langle E_n|$ and the average energy change in the battery is $\text{Tr}[\rho_S H_S] - \text{Tr}[\rho'_S H_S]$. As $S(\rho_S) = S(\rho'_S)$, this is interpreted as work.⁹ ρ'_S is diagonal, so in accordance with Assumption 2 an amount of work $F(\rho'_S) - F(\gamma_S)$ can be extracted from it. The total amount of work extracted is $\text{Tr}[\rho_S H_S] - \text{Tr}[\rho'_S H_S] + F(\rho'_S) - F(\gamma_S) = F(\rho_S) - F(\gamma_S)$.

⁸A similar result appears in [34], however it was based on using a reference system described by a doubly-infinite ladder Hamiltonian. This left open the question if this limit is achievable by a system with a physically realisable Hamiltonian.

⁹This is an interesting situation, because U_{av} acts as a unitary on the system (hence, the energy change is called work). However, the entropy of the battery increases, and one may wonder what is the quality of the extracted work, along the lines of [46].

As U_{av} conserves energy on average, but not strictly, by Assumption 1 it is not a free thermodynamic operation. One can instead ask if it can be achieved by an energy-preserving unitary $V(U_{\text{av}})$ on a larger system that exploits some ancillary system ρ_A . In other words, we are looking for an energy-preserving unitary $V(U_{\text{av}})$ such that

$$\mathcal{E}(\rho_T) := \text{Tr}_A \left[V(U_{\text{av}})(\rho_T \otimes \rho_A) V(U_{\text{av}})^\dagger \right] = U_{\text{av}} \rho_T U_{\text{av}}^\dagger, \quad (6.19)$$

where T denotes the overall system plus battery Hilbert space on which U_{av} acts.

It is easy to show that due to the imposed constraints, the ancillary system ρ_A must carry quantum coherence. In fact, if ρ_A were incoherent, then the left-hand side of Eq. (6.19) would be a time-translation symmetric quantum map, whereas the right-hand side is not.

Now, the crucial point is that Eq. (6.19) cannot hold exactly unless ρ_A contains an unbounded reference. If ρ_A is bounded, then the reduced evolution of ρ_T is not exactly unitary and not all the energy change can be identified with work (see Aside 6.2).

Mathematical Aside 6.2. Unbounded reference is needed

To give a more precise argument that an unbounded reference is needed, we may reason as follows. Let $\rho'_{TA} = V(U_{\text{av}})(\rho_T \otimes \rho_A) V(U_{\text{av}})^\dagger$. Using the invariance of the von Neumann entropy under unitaries,

$$\begin{aligned} I(\rho'_{TA}) &= S(\rho'_A) + S(\rho'_T) - S(\rho'_{TA}) = S(\rho'_A) + S(\rho'_T) - S(\rho_T) - S(\rho_A) \\ &= S(\rho'_A) - S(\rho_A) = \beta(F(\rho_A) - F(\rho'_A)). \end{aligned}$$

In the last step we used that the overall average energy is conserved (because overall energy is strictly conserved) and moreover the average energy of T is conserved; from this it follows that the average energy on the ancilla is conserved as well. We cannot allow the free energy of the ancilla to go down, otherwise one could unsurprisingly break the free energy bound of Assumption 2. $F(\rho_A) \leq F(\rho'_A)$ implies, from the non-negativity of mutual information, $I(\rho'_{TA}) = 0$ and $S(\rho'_A) = S(\rho_A)$. Hence $V(U_{\text{av}})$ must factorise as $V(U_{\text{av}}) = V_1 \otimes V_2$ and further, by assumption, $V_1 = U_{\text{av}}$, so V_1 is not strictly energy-preserving.¹⁰ But this is not possible, because from the fact that $V(U_{\text{av}})$ is strictly energy-preserving we can prove that both V_1 and V_2 must have this property. To see this, recall that a unitary U is strictly energy preserving if and only if it is preserving average energy on every state, as it is clear from

$$\text{Tr} [\rho(U^\dagger H U - H)] = 0 \quad \forall \rho \Leftrightarrow [U, H] = 0, \quad (6.20)$$

if H is the Hamiltonian of the system. Moreover, notice that we can apply $V(U_{\text{av}})$ on all states of the form $\mathbb{I} \otimes \rho$ or $\rho \otimes \mathbb{I}$ and, using the strict energy conservation of $V(U_{\text{av}})$, deduce the strict energy conservation of V_2 and V_1 , respectively.

Hence, the right-hand side of Eq. (6.19) cannot be a unitary if ρ_A contains only a bounded reference frame. In fact, Eq. (6.19) can only hold as a limit case of using a larger and larger coherence resource. In summary, Assumptions 1-3 together with the

identification of work with energy change during unitary processes, imply that without an unbounded reference the work extraction protocol from Refs. [74, 94] cannot extract an amount of work equal to $\Delta F(\rho_S)$ from a state with coherence.

In fact, the argument is rather general and can be summarised as follows. In order to extract all the free energy from a state ρ_S one needs to transform it into a thermal state. If ρ_S has quantum coherence, this cannot be achieved by only changing the energy spectrum of H_S , but also requires the rotation of the energy eigenbasis, so that the system is incoherent at the end of the transformation. This can be performed perfectly only with the aid of an unbounded reference frame, because it involves unitaries that do not strictly conserve energy.¹¹

6.4.2 Extracting work arbitrarily close to the free energy difference

In accordance with Assumption 2, from the diagonal state $D(\rho_S)$ (that has the same energy occupations of ρ_S , but no coherence) one can extract $\Delta F(D(\rho_S))$. Hence, the extraction of the full free energy $\Delta F(\rho_S)$ from a state ρ_S is equivalent to the possibility of extracting $F(\rho_S) - F(D(\rho_S))$ from the coherence of ρ_S . Notice that this quantity coincides with $kTA(\rho_S)$, where $A(\rho_S) = S(\rho_S||D(\rho_S))$ is a known measure of quantum coherence (Lemma 2.44), and it quantifies the amount of free energy stored in coherence (see Eq. (4.14)). Hence, the amount of work that needs to be extracted on average from the coherence of a quantum state to achieve the free energy extraction limit for arbitrary quantum states is

$$W_{\text{coh}}(\rho_S) = kTA(\rho_S). \quad (6.21)$$

A key fact about the Carnot efficiency is that, despite being achieved only by ideal heat engines that do not actually exist in Nature, we can get arbitrarily close to it through a sequence of real engines. In a similar spirit, we now construct a sequence of bounded thermal machines getting arbitrarily close to the coherence to work conversion limit set by Eq. (6.21). The main result of this section can be summarised in a non-technical way as follows:

Theorem 1. There exists a sequence of bounded thermal machines approaching the ideal coherence to work conversion of Eq. (6.21) with arbitrarily high probability of success and with an arbitrarily small change in the quality parameters. The limit case is reversible.

As an immediate consequence of the fact that the limit case is reversible we have:

Corollary 6.2. Eq. (6.21) provides the ultimate limit of coherence to average work conversion.

¹¹A useful point of view is also given by the theory of quantum reference frames and recovery maps [38, 103].

In the remaining part of this section we give more details about the result above, first of all specifying the technical claim and then the main steps of the proof (the details of calculations can be found in the mathematical aside following this discussion). We consider a sequence of reference states ρ_R that approach a classical reference. An arbitrary reference state ρ_R will be described by two parameters $(\langle\bar{\Delta}\rangle, M)$ according to Definition 6.1.

We will now show how to perform the protocol described in the previous section to extract from any pure state $|\psi\rangle$ an amount of work per copy arbitrarily close to the free energy difference $\Delta F(|\psi\rangle)$, while succeeding with arbitrarily high probability and changing the quality of the reference only by a negligible amount. For simplicity, define $f(x) = -x - kT h_2(x)$, where $h_2(\cdot)$ denotes the binary entropy. Theorem 1 can be now made technically precise as follows:

Theorem 1'. Let ρ_R be an arbitrary reference state described by $(\langle\bar{\Delta}\rangle, M)$. In the presence of a thermal bath at temperature T and if M is large enough, there exists a protocol individually extracting from M copies of $|\psi\rangle$ [given by Eq. (6.7)] on average an amount of work $M\langle W\rangle$, with

$$\langle W\rangle \geq \Delta F(|\psi\rangle) - f[2p(1-p)(1-\langle\bar{\Delta}\rangle)] - O(M^{-1/3}).$$

The probability of success p_{succ} of the protocol is

$$p_{\text{succ}} \gtrsim [1 - 2p(1-p)(1-\langle\bar{\Delta}\rangle)]^M,$$

and it changes the quality parameters of the reference as follows:

$$\delta M = 0, \quad |\delta\langle\bar{\Delta}\rangle| \leq 2\sqrt{1 - p_{\text{succ}}}.$$

Before presenting the proof of this theorem, let us first comment on its scope. Note that the same result holds when a reference $(\langle\bar{\Delta}\rangle, M)$ is used a number of times $M' < M$, as long as $M' \gg 1$ (this will be clear from the proof). In the case in which $M' > M$, we can apply the theorem every M uses of the reference. The changes in the quality parameters will eventually sum up, but the theorem gives a bound on them. Also, it will be clear from the proof that failure of the protocol implies a destruction of the coherence properties of the reference.

We now prove the theorem by constructing an explicit variation of protocol introduced in Sec. 6.3 and showing that it performs as stated. Recall that by an energy conserving unitary we can rotate $|\psi\rangle$ around the Z axis of the Bloch sphere. Hence, without loss of generality, we can set $\varphi = 0$ in Eq. (6.7). We then perform steps (1) and (2) of the protocol described in Sec. 6.3 M times, i.e., individually processing each of M copies of $|\psi\rangle$ using a reference ρ_R described by $(\langle\bar{\Delta}\rangle, M)$. The choice of ρ_R ensures that during this process the reference state will have no population in the ground state, and so $\langle\bar{\Delta}\rangle$ will stay constant. Then, the final state of the reference is described with probability p_1^M by

$\rho_{R,1} = A_1^M \rho_R A_1^{\dagger M}$, where $p_1 = (1 - 2p(1 - p)(1 - \langle \bar{\Delta} \rangle))$.¹² Notice that having access to a reference described by parameters $\langle \bar{\Delta} \rangle$ and M such that $M(1 - \langle \bar{\Delta} \rangle) \rightarrow 0$, the probability p_1^M can be made arbitrarily close to 1. This happens because by taking $\langle \bar{\Delta} \rangle$ close enough to 1, we can get arbitrarily close to unitary evolution of a system state $|\psi\rangle$ to a pure, incoherent state $|1\rangle$.

Next, we repump the reference $\bar{M} + s\sigma_M^{4/3}$ times, where $\bar{M} = M(1 - p)$, $\sigma_M = \sqrt{Mp(1 - p)}$ and $s > 0$. This guarantees that the reference has arbitrarily small population in states $\{|0\rangle \dots |M\rangle\}$, so that by performing a measurement we can project the reference to a state ρ_R'' with support on the subspace spanned by $\{|i\rangle\}_{i>M}$ with arbitrarily high probability (s fixes the confidence level, see mathematical aside for details). More precisely, after repeating steps (1) and (2) of the protocol M times, repumping and measuring as explained above, the reference is described by a state ρ_R'' with probability (see Aside 6.3)

$$p_{\text{succ}} \geq [1 - 2p(1 - p)(1 - \langle \bar{\Delta} \rangle)]^M \mathbb{E}_s(M^{1/6}), \quad (6.22)$$

where $\mathbb{E}_s(x) = \text{erf}(sx/\sqrt{2})$ and erf denotes the error function. The final state is given by ρ_R'' , described by $(\langle \bar{\Delta} \rangle'', M'')$, where $M'' = M$ and by the gentle measurement lemma

$$|\delta \langle \bar{\Delta} \rangle| := |\langle \bar{\Delta} \rangle'' - \langle \bar{\Delta} \rangle| \leq 2\sqrt{1 - p_{\text{succ}}} \leq 2\sqrt{1 - p_1^M \mathbb{E}_s(M^{1/6})}. \quad (6.23)$$

Notice that by taking s large enough (but finite) we can make the factor $\mathbb{E}_s(M^{1/6})$ in the previous two equations arbitrarily close to 1, $\mathbb{E}_s(M^{1/6}) \approx 1$. In the appropriately chosen limit $\langle \bar{\Delta} \rangle \rightarrow 1$ and $M \rightarrow \infty$ the quality parameters of the reference state are then unchanged with probability 1. Let us also note that the average cost of the measurement W_E described above is bounded by $kTh_2(p_{\text{succ}})$.

We have just shown that following the procedure above we can guarantee arbitrarily close repeatability with arbitrary confidence level. Hence, we now proceed to proving that it also allows for extracting an average amount of work per system arbitrarily close to the free energy difference $\Delta F(|\psi\rangle)$. To see this, note that after repeating the protocol on M copies of $|\psi\rangle$ we are left with M copies of a state $D(\rho_S')$ from Eq. (6.10) with q given by Eq. (6.12), $q = 1 - 2p(1 - p)(1 - \langle \bar{\Delta} \rangle)$. This state is diagonal in the energy eigenbasis and the average work $\langle \tilde{W} \rangle$ extracted from it is given by $\Delta F(D(\rho_S'))$:

$$\langle \tilde{W} \rangle = 1 + kT \log Z - 2p(1 - p)(1 - \langle \bar{\Delta} \rangle) - kTh_2(2p(1 - p)(1 - \langle \bar{\Delta} \rangle)), \quad (6.24)$$

where as before $h_2(\cdot)$ denotes the binary entropy. By choosing M large enough, we can ensure that the extracted work is arbitrarily peaked around the average given by the above equation. This ensures that when we need to repump the reference, we actually have enough work to invest to do it. The repumping costs $\bar{M} + s\sigma_M^{4/3}$ units of extracted work and the cost of measurement W_E is independent from M . Hence, the net gain per

¹²Focusing on this outcome simplifies the analysis, but it also suggests that the bounds derived are not tight. However, this is sufficient to capture the $\langle \bar{\Delta} \rangle \rightarrow 1$ limit.

processed copy of $|\psi\rangle$ is given by

$$\langle \tilde{W} \rangle - \frac{(\bar{M} + s\sigma_M^{4/3}) + W_E}{M} = \langle W \rangle - O(M^{-1/3}), \quad (6.25)$$

where

$$\langle W \rangle = \Delta F(|\psi\rangle) - 2p(1-p)(1 - \langle \bar{\Delta} \rangle) - kTh_2(2p(1-p)(1 - \langle \bar{\Delta} \rangle)). \quad (6.26)$$

Therefore, the deficit per copy scales as $M^{-1/3}$ and by choosing M large enough it can be made arbitrarily small. Moreover, the previous equation gives us the relation between the quality of the reference and the average extracted work, showing that $\langle W \rangle \rightarrow \Delta F(|\psi\rangle)$ as $\langle \bar{\Delta} \rangle \rightarrow 1, M \rightarrow \infty, M(1 - \langle \bar{\Delta} \rangle) \rightarrow 0$.

We conclude that it is possible, with arbitrarily large success probability, to extract an amount of work arbitrarily close to the free energy change from a pure state with coherence in energy eigenbasis, while processing it individually and properly taking account of all the resources used, i.e., ensuring arbitrarily exact repeatability.

Mathematical Aside 6.3. Details of proof of Theorem 1'

We provide here the details of the repumping protocol. We start from a generic reference state ρ_R such that $\text{supp}(\rho_R) \cap \text{span}\{|0\rangle, \dots, |M\rangle\} = \emptyset$, where $|i\rangle$ are eigenstates of the reference Hamiltonian. We impose the requirements $Mp \gg 1$ and $M(1-p) \gg 1$, where p is fixed by Eq. (6.7).

We now compute the probability of the occurrence of the Kraus A_1 on a generic reference state σ . From Eq. (6.14) we obtain

$$p_1(\sigma) := \text{Tr} [A_1 \sigma A_1^\dagger] = 1 - 2p(1-p)(1 - \text{Tr} [\bar{\Delta} \sigma]),$$

where recall that $\bar{\Delta} = (\Delta + \Delta^\dagger)/2$. Define the state of the reference after individually performing work extraction on $n \geq 1$ qubits through the following recurrence formula

$$\rho_R^{(n)} := A_0 \rho_R^{(n-1)} A_0^\dagger + A_1 \rho_R^{(n-1)} A_1^\dagger, \quad (6.27)$$

where $\rho_R^{(0)} = \rho_R$. Because ρ_R has initially no support in the first M energy levels, we can extract work from M qubits before there is any overlap with the ground state. In other words, $\langle 0 | \rho_R^{(n)} | 0 \rangle = 0, \quad \forall n \in \{1, \dots, M\}$. The previous formula, together with Eq. (6.16), implies that $\bar{\Delta}$ is conserved throughout the protocol. Hence we deduce that

$$\text{Tr} [A_1^M \rho_R A_1^{\dagger M}] = p_1^M(\rho_R) = (1 - 2p(1-p)(1 - \langle \bar{\Delta} \rangle))^M.$$

For notational convenience, we will now drop the explicit dependence of p_1 on ρ_R (initial state of the reference). Using Eq. (6.27) we have

$$\rho_R^{(M)} = p_1^M \rho_{R,1} + (1 - p_1^M) \mathcal{E}_{\text{else}}^{(M)}(\rho_R), \quad (6.28)$$

where $\mathcal{E}_{\text{else}}^{(M)}$ contains all strings of A_0 's and A_1 's different from the string consisting only

of A_1 's and $\rho_{R,1} = A_1^M \rho_R A_1^{\dagger M} / p_1^M$. We can now compute A_1^M :

$$A_1^M = \sum_{k=0}^M \binom{M}{k} p^{M-k} (1-p)^k \Delta^{\dagger k}.$$

We see that A_1^M is binomially distributed in the number of lowering operations $\Delta^\dagger$. The average number of lowerings is $\bar{M} = M(1-p)$ and the standard deviation is $\sigma_M = \sqrt{Mp(1-p)}$. We can perform a number of repumpings as in Eq. (6.11). Let us denote this operation by $\mathcal{P}$. We have chosen M sufficiently large so that the confidence levels associated to σ_M are approximately gaussian. Hence, we can repump the reference $\bar{M} + s\sigma_M^{4/3}$ times, which guarantees that the reference has arbitrarily small population in states $|0\rangle \dots |M\rangle$ with a confidence level controlled by $s > 0$ and increasing with M . More precisely, if P_M is the projector on the subspace spanned by $\{|0\rangle, \dots, |M\rangle\}$ and $P_M^\perp = \mathbb{I} - P_M$, using the gaussian approximation to a binomial,

$$\text{Tr} [P_M^\perp \mathcal{P}(\rho_{R,1})] \geq \text{erf}(sM^{1/6}/\sqrt{2}) := \mathbb{E}_s(M^{1/6}), \quad (6.29)$$

where $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt$ denotes the error function [for a normal distribution $N(x)$, with average μ and standard deviation σ , the area within $[-x, x]$ reads $\text{erf}\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)$]. Now, using Eq. (6.28) and Eq. (6.29)

$$p_{\text{succ}} := \text{Tr} [P_M^\perp \mathcal{P}(\rho_R^{(M)})] \geq p_1^M \mathbb{E}_s(M^{1/6}). \quad (6.30)$$

This implies that in performing the two-outcome measurement $\{P_M, P_M^\perp\}$ we would find the outcome $P_M^\perp$ with probability bounded by Eq. (6.30).

Performing such a measurement guarantees that the final state of the reference will have no support on a subspace spanned by $\{|0\rangle \dots |M\rangle\}$, like the initial state. However, performing a selective measurement has a thermodynamic cost that we have to take into account. More precisely, the measurement can be performed using an ancillary memory qubit system A described by trivial Hamiltonian $H_A = 0$. Then, taking the initial state of A to be a pure state $|0\rangle$, we can perform an operation on the joint reference-ancillary state described by the Kraus operators $M_1 = P_M^\perp \otimes \mathbb{I}$ and $M_2 = P_M \otimes \sigma_x$. This operation is energy conserving, as the Kraus operators commute with the total Hamiltonian $H_R + H_A$. Hence, it is free of thermodynamic cost. Now the projective measurement on states $|0\rangle$ and $|1\rangle$ can be performed on the ancillary memory system. Observing the result 0 will project the reference on a subspace $P_M^\perp$, whereas observing the result 1 will project the reference on P_M . The thermodynamic cost associated with this projective measurement is the cost of erasing the memory system afterwards. This is given by $W_E = kT h_2(p_{\text{succ}})$, which can be made arbitrarily small as $p_{\text{succ}} \rightarrow 1$. Notice that we only needed to use a classical memory to record the measurement outcome, which is not in contrast with assumption 3 of Section 6.3. Also note that this cost has to be paid only after extracting work from M copies, hence the cost per copy scales as M^{-1} .

Define

$$\rho_R'' := \frac{P_M^\perp \mathcal{P}(\rho_R^{(M)}) P_M^\perp}{p_{\text{succ}}}.$$

Now, using the gentle measurement lemma [104, 105], Eq. (6.30) also implies

$$\left\| \rho_R'' - \mathcal{P}(\rho_R^{(M)}) \right\| \leq 2\sqrt{1 - p_{\text{succ}}}. \quad (6.31)$$

From Eq. (6.31), and the following characterization of the trace norm (see [26])

$$\|\rho - \sigma\| = \max_{0 \leq A \leq \mathbb{I}} \text{Tr} [A(\rho - \sigma)]$$

we find that

$$\text{Tr} [\bar{\Delta}(\rho_R'' - \mathcal{P}(\rho_R^{(M)}))] \geq -2\sqrt{1 - p_{\text{succ}}}.$$

Using the fact that $\langle \bar{\Delta} \rangle$ is conserved in the protocol, up to the measurement, the last inequality can be rewritten as

$$\text{Tr} [\bar{\Delta}(\rho_R - \rho_R'')] \leq 2\sqrt{1 - p_{\text{succ}}}.$$

Exchanging the roles of ρ_R and ρ_R'' and introducing $\delta\langle \bar{\Delta} \rangle = \text{Tr} [\bar{\Delta}\rho_R''] - \text{Tr} [\bar{\Delta}\rho_R]$, we conclude

$$|\delta\langle \bar{\Delta} \rangle| \leq 2\sqrt{1 - p_{\text{succ}}}.$$

Using Eq. (6.30), this bounds the maximum allowed change of the quality parameter of the reference.

6.5 Extracting work with perfect repeatability and bounded thermal machines

In the previous section we have shown how to extract as work all free energy of a pure quantum state with coherence. However we allowed for

1. The limit case of an unbounded thermal machine, $\langle \bar{\Delta} \rangle \rightarrow 1$.
2. An asymptotic protocol individually processing a large number M of copies of the system.

These assumptions may be too strong if the reference itself is a microscopic system involved in the thermodynamic processing and exclude the applicability to single-shot scenarios. What if we only want to process a small number of systems? This requires us to go beyond the results of the previous section.

Moreover, even if we only want to release the first of the two assumptions, i.e., put a bound on the coherence properties of the reference, we are still left with open questions. In this case the general result stated by Theorem 1 is applicable, however the work extraction protocols presented always entail a failure probability $1 - p_{\text{succ}}$ that can lead to a complete destruction of the coherent properties of the reference. Even if this probability is relatively small, we may not be willing to take this risk. Also, the reference inevitably

deteriorates, even if by a small amount bounded by Eq. (6.23). A crucial question is then: are there work extraction protocols with $\langle \bar{\Delta} \rangle < 1$ such that $\delta \langle \bar{\Delta} \rangle = 0$ and $p_{\text{succ}} = 1$? In other words, can we extract work from coherence using a protocol that *never* fails and gives back the thermal machine with *exactly* the same quality parameters, even if the reference is bounded?

In this section we construct such protocols for both average and single-shot work extraction. These ensure perfect repeatability, but the price we pay is that the average amount of extracted work is strictly smaller than the free energy difference and it is only possible for $\langle \bar{\Delta} \rangle$ above a certain threshold value $\bar{\Delta}_{\text{crit}}$. In the case of single-shot work extraction we show similarly that there exists a threshold over which the reference allows us to outperform the single-shot protocol with no coherence. For clarity of the discussion, we focus on the paradigmatic case of the class of states $|\gamma\rangle$ introduced in Eq. (6.8).

6.5.1 Average work extraction

As we have seen in Chapter 4, in absence of an external source of coherence no work can be extracted from the state $|\gamma\rangle$ on average [5, 81]. However, if we allow for a repeatable use of the reference, positive work yield can be obtained. In order to achieve this, during step (2) of the protocol we perform average work extraction from the state $D(\rho'_S)$ specified by Eq. (6.10). As $D(\rho'_S)$ is diagonal in the energy eigenbasis, Assumption 2 applies. Therefore, the average work yield is given by the free energy difference $\Delta F(D(\rho'_S))$. To ensure perfect repeatability we repump the reference at each run, so that if $\langle 0 | \rho_R | 0 \rangle = 0$, then $\langle 0 | \rho_R'' | 0 \rangle = 0$, and the reference quality parameters do not change. The repumping requires a unit of work, so that the work extracted on average during one run of the protocol is

$$\langle W \rangle = q + kT(\log Z_S - h_2(q)) - 1. \quad (6.32)$$

The connection between the properties of the reference and the work yield is given by Eq. (6.32) together with Eq. (6.12) (where $R_{00} = 0$ and $p = r$). As $\langle \bar{\Delta} \rangle \rightarrow 1$, if $R_{00} = 0$ then $\langle W \rangle \rightarrow kT \log Z_S = -\Delta F(|0\rangle\langle 0|)$ (so we do not achieve $\Delta F(|\gamma\rangle)$).

In Fig. 6.3 we show how much work $\langle W \rangle$ can be unlocked through our protocol as a function of the quality of the reference $\langle \bar{\Delta} \rangle$ and the thermal occupation r of the excited state. The graph shows that the quality of the reference needs to be above a certain threshold in order to get positive average work yield. As expected, the advantage is the most significant for high r , because the states $|\gamma\rangle$ and γ_S differ most in this case or, in other words, the amount of coherence to be unlocked is higher.

As already mentioned in Sec. 6.2, in the asymptotic regime of individually processing large number of copies of $|\gamma\rangle$, the fluctuations in the work yield, Eq. (6.32), become negligible. Notice, however, that even if $\langle W \rangle > 0$ we may not be able to perform step (3) every time, as the fluctuations around the average mean that we will not always have enough work to invest in the repumping. To resolve this problem we can follow a strategy analogous to the case of unbounded reference. That is, we repump after having extracted

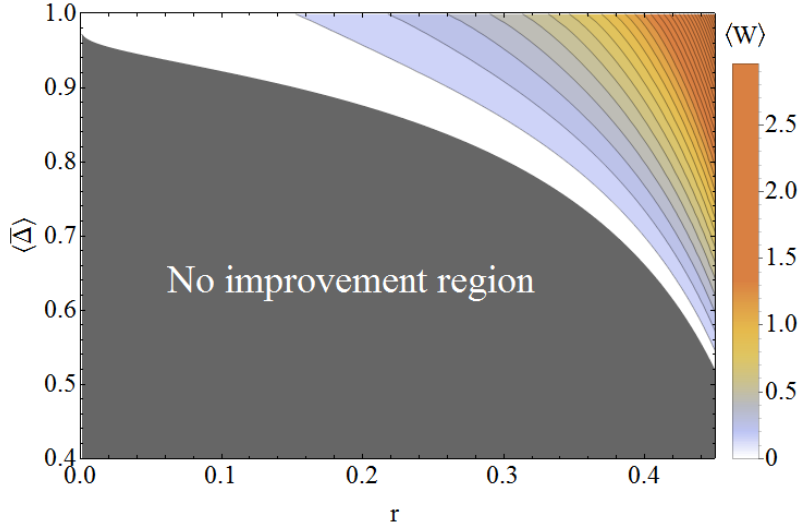


Figure 6.3. Coherence boost to average work extraction from $|\gamma\rangle$. Work can be unlocked from the coherence of the system using a thermal machine that never deteriorates. The quality of the machine, measured by $\langle \bar{\Delta} \rangle$, must be bigger than some threshold value (boundary of the grey region) to ensure $\langle W \rangle > 0$ (r denotes the thermal occupation of the excited state, $r = (1 + e^{1/kT})^{-1}$). Over the threshold, the higher the quality the greater is the average work yield from quantum coherence.

work M times, where M is sufficiently large to neglect the fluctuations around $\langle W \rangle$.¹³ The protocol will be repeatable up to an arbitrarily small probability of failure, if the support of the reference initially starts high enough in the energy ladder. It is important to stress, however, that the “failure” in this case does not entail a destruction of the coherence properties of the reference, as in Sec. 6.4.2. It only requires the investment of extra work in order to ensure perfect repeatability.

6.5.2 Single-shot work extraction

Finally, we proceed to a fully quantum and single-shot protocol for an individual quantum state. This version of the protocol does not assume possessing an unbounded reference nor it requires asymptotic number of runs. In absence of an external source of coherence we can perform ϵ -deterministic work extraction from $|\gamma\rangle$ – as $|\gamma\rangle$ is indistinguishable from γ_S , the results of [46] apply. This means that we can extract $kT \log Z_S$ work with failure probability r or $1 + kT \log Z_S$ with failure probability $1 - r$. We now show that exploiting the reference in a perfectly repeatable way the failure probability for extracting $kT \log Z_S$ can be decreased – and the higher the quality of the reference, the stronger the improvement.

During step (2) of the protocol we perform ϵ -deterministic work extraction from the state $D(\rho'_S)$ specified by Eq. (6.10), in accordance with Assumption 3. With probability q we extract $1 + kT \log Z_S$ work and with probability $1 - q$ our protocol fails. As we need

¹³One can think of alternative protocols as well, in which at every repetition we toss a coin to decide if we repump the reference or not. We do not delve into this, but we expect to find similar results.

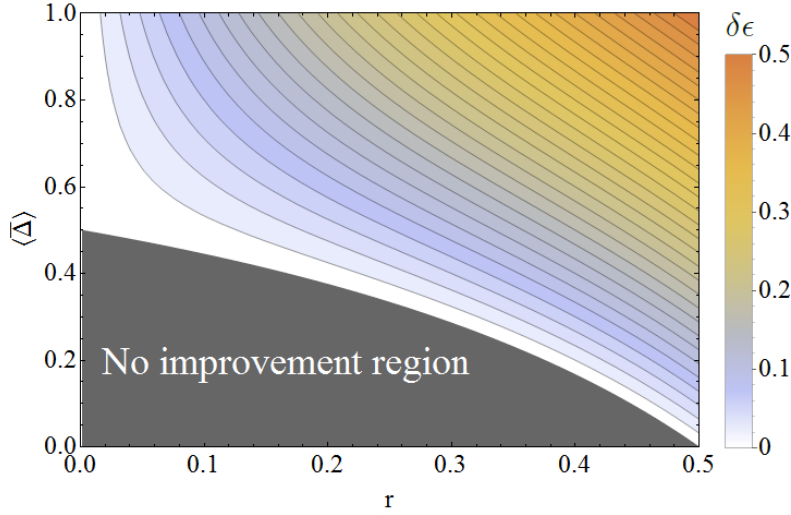


Figure 6.4. Coherence boost to single-shot work extraction from $|\gamma\rangle$. A thermal machine, used in a repeatable way, can exploit the quantum coherence of the system to decrease the failure probability in single-shot work extraction. Similarly to the case of average work extraction, the quality of the machine $\langle\bar{\Delta}\rangle$ must be over some threshold value to lead to any improvement (r denotes the thermal occupation of an excited state). As $\langle\bar{\Delta}\rangle$ increases, the failure probability decreases from r to $r - \delta\epsilon$, down to zero, i.e., to the point when the single-shot work extraction from the pure quantum state $|\gamma\rangle$ becomes fully deterministic.

one unit of work to repump the reference (see Eq. (6.11)), the net gain is $kT \log Z_S$. When the protocol fails, the reference is returned in the state ρ'_R and one has to invest one unit of work to ensure repeatability.

In Fig. 6.4 we present the decrease $\delta\epsilon$ in the failure probability ϵ achieved by our protocol as compared to work extraction from γ_S . We see that if the quality of the reference is high enough, the coherence content of $|\gamma\rangle$ can be exploited to provide an advantage in the work extraction. In the limit of a very high quality (unbounded) reference, $\langle\bar{\Delta}\rangle \rightarrow 1$, the failure probability can be sent to zero, i.e., the work extraction from $|\gamma\rangle$ becomes deterministic (as it is for pure states with no coherence)

6.6 Conclusions

In this chapter we have addressed the following question: how much work can be extracted from a state that is a superposition of energy eigenstates? We argued that this question, within the currently developed theory of thermodynamics of individual quantum systems, is a subtle issue. We showed that the optimal coherence to work conversion can be obtained only in the limit of accessing a reference system with unbounded coherence resources. Although no real reference is unbounded (in the same way in which no heat engines is ideal), we can get arbitrarily close to the limit by means of a sequence of bounded thermal machines.

The access to arbitrarily large resources should be questioned in the regime under

study. Generally speaking, recovering traditional thermodynamical results requires extra assumptions, which all entail some notion of “classicality”, so to effectively make coherence negligible: neglecting the energy fluctuations due to superposition; assuming the existence of a source of coherence that experiences essentially no back-reaction; collectively operating on infinitely many copies of the system.

When the “classicality” assumptions are dropped one after the other, the results are quantitatively different from the thermodynamics of incoherent systems. Nevertheless, we find that the coherence between energy levels can still enhance the performance of work extraction protocols. There exist perfectly repeatable processes extracting on average a larger amount of work than what could be extracted in the absence of coherence; and single-shot protocols in which coherence improves the success probability of work extraction. Although these protocols are better than the correspondent incoherent ones, they do not achieve the performance reached in the classical limit.

We also point out that while dealing with microscopic systems, the accounting of all the resources involved in thermodynamic processes becomes a crucial and non-trivial task. In this regard, we underline the importance of accounting for the resources which make up a thermal machine, and the concept of repeatability, that essentially captures the idea of using these extra resources without degrading them. In particular, the considerations here suggest that a full theory of thermodynamics in the quantum regime will require a better understanding of the accounting of coherence resources, including those found in the thermal machine. We are still far from having a full understanding. We hope to have convinced the reader that the question of the role of quantum coherence in thermodynamic considerations does not admit an easy and immediate answer, and that it is only by appropriately incorporating it into the theoretical framework that we can explore truly quantum mechanical effects.

Remark 6.3 (Open questions). When $p \rightarrow 0$, the reference is operating on an initially incoherent state. So, the quantum channel describing the back-reaction on the reference is a covariant map. However, Eq. (6.16) gives us $\delta\langle\bar{\Delta}\rangle \rightarrow -\text{Re}(R_{01})$, i.e., $\langle\bar{\Delta}\rangle$ is allowed to change. This shows – somehow surprisingly – that the measure of how useful a reference is in protocols using it repeatably is *not* a monotone under covariant maps. This observation naturally leads to various questions: is there a stronger notion – call it *useful coherence* – that is distinct from what is quantified by asymmetry measures? Can we then envisage a “preparatory stage” in which one tries to apply covariant operations on the reference to maximise its useful coherence? Is the ability of time-translation symmetric dynamics to “align phases”¹⁴ an example of a physical phenomenon of wider interest?

¹⁴To increase $\langle\bar{\Delta}\rangle$ the off-diagonal elements must be in phase, whereas this is irrelevant for coherence measures such as the ℓ_1 norm of coherence (i.e. the sum of the absolute values of the off-diagonal elements).

7 Beyond Thermal Operations

We discuss here several open directions that are the object of current research and stem naturally from considerations in this thesis. The results of this chapter should be considered as preliminary discussions of topics currently under investigation. The common theme is, as the title suggests, overcoming various limitations of the Thermal Operations approach to thermodynamics. Here is a summary:

1. In the first part, we will discuss an alternative definition for the set of thermodynamically allowed operations with a clearer operational interpretation in terms of physically realisable toy models. As such, this framework may provide sharper constraints for thermodynamic settings that are closer to applications.
2. In the second part, we will briefly discuss the role of Markovianity and non-Markovianity in preserving coherence. In fact, all considerations so far are valid for general quantum channels. The aim of this investigation is two-fold: on one hand we can hope to obtain sharper constraints for typical physical situations (say, a Markovian thermalisation); on the other hand, by comparing the general bounds and the Markovian ones, one can infer useful information about the role of non-Markovianity in coherence preservation.
3. Finally, we discuss the question of non-commutativity in thermodynamics. This mostly unexplored topic still needs to prove its physical relevance, but from the theoretical point of view is a natural testing ground to probe if our classical ideas about thermodynamics will carry over to the quantum regime.

7.1 Elementary Thermal Operations

Thermal Operations define a general framework for analysing quantum thermodynamic questions. As we argued in Sec. 2.2.2, some of the criticism of this approach may be associated with a misinterpretation of the role and use of the set of free operations in a resource theory. However, some of the criticism is fair. We may summarise it in a positive way saying that one may hope to define a set of free operations that are, in some sense to be made precise, closer to physically realisable situations in which certain experimental procedures are “easy”, whereas others are “hard”. This, ideally, would make the task of connecting the general abstract results to specific implementations easier. In this section we present common criticisms of Thermal Operations and introduce a new

sets of maps whose operational realisation is associated to a particularly simple class of thermodynamic models.

7.1.1 Criticism of Thermal Operations

The framework of Thermal Operations (TOs), introduced in Section 2.2.2, has been criticised in at least two, somehow opposing, ways, that we now present. TOs clearly contain a large set of transformations that can be implemented only through a complete control of the system-bath interaction U . This in general requires a fine control of the microscopic degrees of freedom of the bath, on top of the assumption that any bath Hamiltonian H_B can be engineered; hence, achieving the full set of TOs seems completely unrealistic from an experimental point of view [106].

One may respond that we are interested in “fundamental” limitations, so that by allowing such a large set of transformations we are able to embrace a large variety of experimental situations; which is to say, the constraints derived will still provide necessary conditions, however weak, to practically relevant scenarios. But, conversely, TOs appear in other ways overly restrictive. In particular, the constraint of energy conservation may seem at first glance a serious limitation. In fact, typical experimental situations involve turning on and off some couplings, spending or acquiring work from the system. Hence, to model what is done in the lab, one should in general introduce auxiliary systems (e.g. a field) and keep track of their evolution; however, this becomes cumbersome quickly. A deeper analysis of the connections to experimental implementations is then crucial. A summary of my current understanding can be found in Fig. 7.1.

In this section we aim to make a step towards overcoming the above criticism and clarifying how to connect the resource theory approach to more experimentally-friendly frameworks. Given a finite-dimensional system with Hamiltonian $H_S = \sum_i \hbar \omega_i |i\rangle\langle i|$, we will initially focus on transitions among incoherent states ρ and σ i.e. $[\rho, H_S] = [\sigma, H_S] = 0$. Let $\mathbf{p}$ and $\mathbf{q}$ be the eigenvalues of ρ and σ , representing the occupations of each energy level. Recall Def. 2.35: we denote by $\mathcal{T}$ the set of thermal stochastic processes, i.e., all stochastic matrices T with $T_{i|j} = \langle i | \mathcal{T}(|j\rangle\langle j|) | i \rangle$ for some TO $\mathcal{T}$ (we say that T is *induced* by $\mathcal{T}$). These represent the random energy exchanges between system and bath and do not carry a description of how superpositions among different energy levels evolve. Since, by assumption, no such superpositions are present in ρ and σ , a TO $\mathcal{T}$ with $\mathcal{T}(\rho) = \sigma$ exists if and only if there exists a thermal process T with $T\mathbf{p} = \mathbf{q}$ (see Proposition 2.36).

7.1.2 Elementary Detailed balanced Processes (EDPs)

We focus here on finding a candidate subset of Thermal Operations associated with a physically reasonable model (the “LAB free” set in Fig. 7.1). Notice that, in the context of thermodynamics, a central role is played by the detailed balance condition [69, 107], satisfied by typical thermalisation processes:

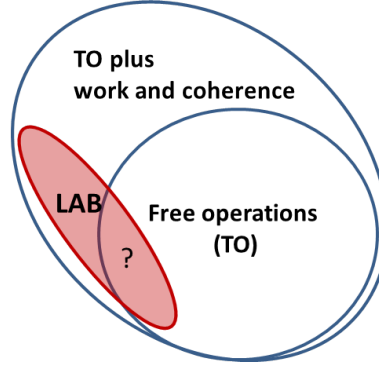


Figure 7.1. Too big, too small? An illustration of where the resource theory stands with respect to laboratory thermodynamics. There are four main regions: 1. *Free thermodynamic operations (TO)*, stuff we could potentially do for free, but typically cannot due to practical limitations; 2. *TO plus work and coherence*, stuff we can do with TO plus some resources, that corresponds to every possible quantum channel (as discussed in the box of Sec. 2.2.2); 3. *LAB thermodynamics*: stuff we actually do in the lab, that splits into two subregion, 3a. *LAB free*, the intersection of LAB with TO, corresponding to things we can actually do in the lab for free (e.g. Jaynes-Cummings model in RWA approximation); and 3b. *LAB not free*, the complementary (in *LAB thermodynamics*) of the previous region, corresponding to operations we do in the lab requiring extra resources (say, work to switch on and off couplings or energy and coherence to do an average energy preserving unitary). The focus of this section is to put forward a candidate for 3a. The two different criticisms can be intuitively understood from the picture.

Definition 7.1 (Detailed Balance). A stochastic map M is called detailed balanced with respect to the thermal state g if

$$\frac{M_{i|j}}{M_{j|i}} = e^{-\beta\hbar(\omega_i - \omega_j)} = \frac{g_i}{g_j}. \quad (7.1)$$

Now, among all maps satisfying detailed balance, many of them will entail a very fine-tuned control of a large number of energy levels at a time. As we are mostly interested in the thermodynamics of single or few quantum systems, we may accept a high level of control. However, it seems physically reasonable to limit interactions to those involving only two energy levels at a time. Then, among all stochastic processes that may describe the random heat exchanges between system and bath, a subset stands out as particularly simple and (potentially) physically motivated:

Definition 7.2 (Elementary Detailed Balanced Processes, or EDPs). They are all stochastic matrices E satisfying two conditions:

1. Only two energy levels of the system are involved.
2. Detailed balance, $E_{i|j} = e^{-\beta\hbar(\omega_i - \omega_j)} E_{j|i}$, is satisfied.

The set of all such stochastic matrices will be denoted by $\mathcal{E}$. More explicitly, every $E \in \mathcal{E}$ has the especially simple structure

$$E = \begin{bmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \dots & E_{i|i} & \dots & E_{i|j} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & E_{j|i} & \dots & E_{j|j} & \dots \\ \ddots & \vdots & \vdots & \vdots & \ddots \end{bmatrix},$$

where $E_{i|j} = E_{j|i}e^{-\beta\hbar(\omega_i-\omega_j)}$ and dots are all zeros for off-diagonal elements and 1 for diagonal elements. Due to stochasticity, if H_S is known an EDP is fully determined by the labels i, j and a single transition probability. This can be chosen to be any $E_{i|j} \in [0, 1]$, if $\omega_j > \omega_i$. One can check that $\mathcal{E} \subset \mathcal{T}$, i.e., all EDPs can be induced by means of TOs:

Lemma 7.3. $\mathcal{E} \subset \mathcal{T}$, i.e., for any EDP there exists a TO inducing it. Conversely, not all thermal processes are elementary detailed balanced processes.

Mathematical Aside 7.1. Proof of Lemma 7.3

Let $|\phi_0\rangle, |\phi_1\rangle$ be two eigenstates of H_S with energies $\hbar\omega_0$ and $\hbar\omega_1$, with $\omega_1 > \omega_0$. Let E be an EDP involving them, fully characterised by the transition probability $E_{0|1} \in [0, 1]$. We now show that $E \in \mathcal{T}$, by explicitly constructing a TO inducing it. Consider a single-mode thermal bath with Hamiltonian $H_B = \sum_{n=0}^{\infty} n\hbar\omega |n\rangle\langle n|$, with $\omega = \omega_1 - \omega_0$. Let the bath be in the state γ_B , with $\gamma_B = e^{-\beta H_B}/Z_B$, where $Z_B = (1 - e^{-\beta\hbar\omega})^{-1}$. Take now the energy-preserving unitary (appearing in [46])

$$U = |\phi_0\rangle\langle\phi_0| \otimes |0\rangle\langle 0| + \sum_{n=1}^{\infty} \sum_{k,k'=0}^1 v_{kk'} |\phi_k\rangle\langle\phi_{k'}| \otimes |n-k\rangle\langle n-k'|,$$

where V (whose elements are $v_{kk'}$) is a 2 by 2 unitary. Hence, by definition,

$$\rho \mapsto \text{Tr}_B [U(\rho \otimes \gamma_B)U^\dagger] := \mathcal{T}(\rho),$$

is a TO. One can directly compute the induced transition probabilities of the stochastic process T induced by $\mathcal{T}$ on the energy eigenbasis:

$$T_{1|0} = e^{-\beta\hbar\omega}|v_{10}|^2, \quad T_{0|1} = |v_{01}|^2,$$

the others being determined by the condition of stochasticity (that follows from the unitarity of V). We can take V of the form

$$V = \begin{bmatrix} \cos(x) & -i \sin(x) \\ -i \sin(x) & \cos(x) \end{bmatrix}.$$

Then for any $E_{0|1} \in [0, 1]$ we can choose x such that $\sin^2(x) = E_{0|1}$, so that $T_{0|1} = E_{0|1}$. Hence we realised every EDP through a TO, which implies $\mathcal{E} \subseteq \mathcal{T}$. The inclusion is strict, because TOs can act on more than two levels and also do not need to satisfy the detailed balance condition ([24], Supplementary Note 6).

The heat exchanges described by $\mathcal{E}$ are far simpler than the generic processes in $\mathcal{T}$. In fact, each EDP is defined by the two levels it acts on plus a single parameter. Of course, mathematical simplicity is not by itself sufficient. For example, the interactions we used to prove Lemma 7.3 involve non-standard couplings (see Appendix E.3 of [34]). Hence, the question arises: can we induce all EDPs using TOs associated to a “natural” physical model? This is what we will explore next.

7.1.3 The Jaynes-Cummings model approximates all EDPs

One of the core descriptions of the interaction between matter and radiation is given by the Jaynes-Cummings model, and so we start investigating the previous question within it. For simplicity, consider a system whose relevant transition frequencies are all well separated from each other. Assume one is allowed to couple every transition of the system to a single-mode bosonic bath in a thermal state through a resonant Jaynes-Cummings coupling in RWA approximation, $H_{JC} = g(\sigma_+ \otimes a + \sigma_- \otimes a^\dagger)$, for a time t . Here $a^\dagger, a$ are creation/annihilation operators on the bath and $\sigma_\pm$ excite/de-excite a transition $\omega := \omega_1 - \omega_0 > 0$ on the system. Let $|\phi_k\rangle, k = 0, 1$, be the eigenstates of H_S associated to the two levels of energy $\hbar\omega_0$ and $\hbar\omega_1$. Moreover, $H_B = \sum_{n=0}^{\infty} n\hbar\omega |n\rangle\langle n|$. One can compute ([34], Appendix E.2)

$$e^{-\frac{it}{\hbar}H_{JC}} = \sum_{n=1}^{\infty} \sum_{k,k'=0}^1 u_{k,k'}^{(n)}(s) |\phi_k\rangle\langle\phi_{k'}| \otimes |n-k\rangle\langle n-k'| + |\phi_0\rangle\langle\phi_0| \otimes |0\rangle\langle 0|, \quad (7.2)$$

where $s = gt/\hbar$ and, for each n , $u_{k,k'}^{(n)}(s)$ are matrix elements of the unitary

$$U^{(n)}(s) = \begin{bmatrix} \cos(s\sqrt{n}) & -i\sin(s\sqrt{n}) \\ -i\sin(s\sqrt{n}) & \cos(s\sqrt{n}) \end{bmatrix}.$$

Take system and bath to be in the initial state $\rho \otimes e^{-\beta H_B}/Z_B$, where $Z_B = (1 - e^{-\beta\hbar\omega})^{-1}$. One then has that the dynamics of the system is described as

$$\rho \mapsto \text{Tr}_B \left[e^{-\frac{it}{\hbar}H_{JC}} (\rho \otimes e^{-\beta H_B}/Z_B) e^{\frac{it}{\hbar}H_{JC}} \right],$$

so it is a Thermal Operation. A standard calculation provides the induced stochastic processes:

$$J_{1|0}(s) = \sum_{n=1}^{\infty} \sin^2(s\sqrt{n})g_n, \quad J_{0|1}(s) = \sum_{n=1}^{\infty} \sin^2(s\sqrt{n})g_{n-1}, \quad (7.3)$$

where $g_n = e^{-\beta\hbar\omega n}/Z_B$ is the occupation of the n -th energy level of the bath and $s = gt/\hbar$.¹ Also, $J_{0|0} = 1 - J_{1|0}$, $J_{1|1} = 1 - J_{0|1}$. One has $J_{1|0}/J_{0|1} = e^{-\beta\hbar\omega}$, i.e. J is an EDP, defined by a single control, s . The question then arises, to what extent can *all* $E \in \mathcal{E}$ be

¹For any s , one can take g small enough and t large enough to avoid the short times/strong couplings regime where the model breaks down.

achieved? The independent parameter for a generic EDP on two levels can be chosen to be the de-exciting probability $E_{0|1}$. If, for every $E_{0|1} \in [0, 1]$, there exists an s such that $J_{0|1}(s) = E_{0|1}$, then all EDPs can be achieved. We have

Lemma 7.4. *Let H_S be a non-degenerate Hamiltonian with well-separated spacings. Then, the Jaynes-Cummings interactions in RWA approximation with a single-mode bosonic bath induce EDPs. In fact, in the low-temperature limit, all EDPs can be achieved.*

Proof. The above discussion shows that every transformation within the resonant Jaynes-Cummings model in RWA approximation gives an EDP.

To investigate the low temperature limit notice that we only need to show that in such limit $J_{0|1}(s)$ can achieve all values in $[0, 1]$. For every s we have

$$J_{0|1}(s) \geq (1 - e^{-\beta\hbar\omega}) \sin^2(s).$$

At $s = 0$, in fact, equality holds. By continuity of $J_{0|1}(s)$ and the previous inequality, we see that all values in $[0, 1]$ can be achieved, varying s , in the limit $\beta \rightarrow \infty$. Hence, at zero temperature, all EDPs can be induced within the Jaynes-Cummings model, by varying s . ■

One may be tempted to hope that all EDPs can be achieved within the Jaynes-Cummings model at all temperatures. Analytically, one immediately notices that $J_{0|1}(s) < 1$ for all times s . However, this does not exclude that there is a sequence of s_i such that $J_{0|1}(s_i)$ gets arbitrarily close to 1, i.e., such that we can approximate EDPs arbitrarily well within the Jaynes-Cummings model. As the dynamics in s is very chaotic, this cannot be ruled out numerically. What we need is a bound on $J_{0|1}$ independent of s . In the following lemma we prove such bound:

Lemma 7.5. *For the Jaynes-Cummings model, set $\bar{\beta} = \beta\hbar\omega$. Then for every s*

$$\begin{aligned} J_{0|1}(s) &\leq \frac{1}{16} \left(8e^{-\bar{\beta}} - e^{2\bar{\beta}} + e^{3\bar{\beta}} + 8 \right), \text{ for } \bar{\beta} \in [0, \log(4)/3], \\ J_{0|1}(s) &\leq e^{-4\bar{\beta}} - e^{-3\bar{\beta}} + 1 \quad \text{for } \bar{\beta} \geq \log(4)/3. \end{aligned}$$

The usefulness of these bounds is that they prove, for any fixed (inverse) temperature $\beta \in (0, +\infty)$, that there is a constant $C_\beta \in (0, 1)$ such that $J_{0|1} < 1 - C_\beta$ for all s . So, the Jaynes-Cummings model at finite temperature cannot achieve all EDPs, nor arbitrary approximations of them:

Corollary 7.6. *For any fixed $\beta \in (0, +\infty)$, the Jaynes-Cummings cannot induce arbitrary close approximations of every EDP.*

Proof of Lemma 7.5. Consider the bound on $J_{0|1}(s)$ constructed following these steps:

1. Split the series for $J_{0|1}$ in Eq. (7.3) into a finite sum F up to m , plus a residue R . In the residue, bound each factor $\sin^2(s\sqrt{n})$ with 1. Then one has $R = e^{-m\beta\omega}$.

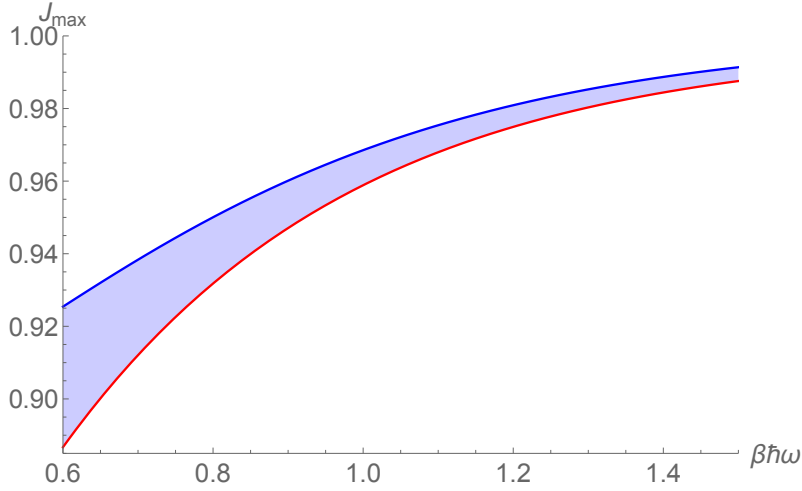


Figure 7.2. Realising EDPs in the simplest Jaynes-Cummings model: to achieve every elementary detailed balanced process (EDP), one needs to be able to obtain all de-exciting probabilities $E_{i|j} \in [0, 1]$, $\omega = \omega_j - \omega_i > 0$. We prove one can realise every transition probability within $[0, J_{\max}(\beta\hbar\omega)]$, where $J_{\max}(\beta\hbar\omega)$ lies somewhere within the shaded area. Hence, far from the high temperature limit, almost all EDPs can be achieved within the Jaynes-Cummings model.

2. In F , bound every oscillating term with irrational frequency as $\sin^2(s\sqrt{n}) \leq 1$.

This provides a bound of $J_{0|1}(s)$ with a periodic function of s , which can then be analysed simply. For $m = 4$, the function has one global maximum at $s = \pi/2$ when $\bar{\beta} \geq \log(4)/3$. On the other hand, when $\bar{\beta} < \log(4)/3$ it has two global maxima at $s = \pm \arccos(-e^{3\bar{\beta}}/4)/2$. The values achieved at the maxima give the bounds of Lemma 7.5. ■

On the other hand, a rough lower bound (good when temperatures are not too high) of the achievable $J_{0|1}$ can be obtained by truncating the sum in Eq. (7.3) at some finite $m_{\max}$, and setting every other term to zero. We take $m_{\max} = 12$. Then numerics suggest to choose $s = 98.92$.

These results imply that in the Jaynes-Cummings model one can reach all de-exciting probabilities in the interval $[0, J_{\max}(\beta\hbar\omega)]$, where $J_{\max}(\beta\hbar\omega)$ lies in the region presented in Figure 7.2. We saw that when $\beta \rightarrow \infty$ (the zero temperature limit) $J_{\max} \rightarrow 1$, so the Jaynes-Cummings model gives all EDPs. We now see that also the finite temperature scaling is rather favourable: at room temperature $T_B = 300K$ and frequencies of 10^{13} Hz or above, and at millikelvin temperatures with frequencies of around 10^8 Hz, one has $J_{\max}(\beta\hbar\omega) > 0.98$.

We conclude that, for a wide interval of reasonable parameters, almost all EDPs can be realised within a simple subset of TOs corresponding to a physically reasonable model, with no need to implement general unitaries or engineering thermal states with arbitrary Hamiltonian. In this sense, EDPs are an operationally motivated set of stochastic maps to allow in the theory. Of course, one still requires considerable frequency control as we

must be able to separately couple to every transition frequency of the system. This is feasible only if we are interested in the thermodynamics of small enough systems.

7.1.4 Thermalisation models and Markovian EDPs

To strengthen the claim that EDPs are an operationally motivated set of stochastic matrices, we investigate the connection to thermalisation models and the master equation formalism, widely used in quantum thermodynamics [108].

Consider a *collision model* of thermalisation of a system in the presence of a large thermal bath [109]. A thermal particle from the bath approaches, interacts with a two-level subsystem and scatters away; the interaction conserves energy and the particle is lost in the bath [110]. Each “collision” is then described, at the level of populations, as an EDP. Reasoning as in [110], one finds that the combined effect of many identical weak interactions on each two-level subsystem, initially described by a population $\mathbf{p}(0)$, leads to an exponential relaxation:

$$\mathbf{p}(t) = e^{-t/\xi} \mathbf{p}(0) + N(1 - e^{-t/\xi}) \mathbf{g}, \quad (7.4)$$

where $\xi > 0$ and N is the normalisation of $\mathbf{p}(0)$.

This can be seen following a similar strategy to [110]. Let the relevant two-level subsystem, with energies $\hbar\omega_0, \hbar\omega_1$, be described by the (possibly unnormalised) distribution $\mathbf{p}(0) := (p_0(0), p_1(0))$. Without loss of generality, take $\omega_0 = 0$ and $\omega_1 = \omega$. Let $\mathbf{p}(n) := E^n \mathbf{p}(0)$, with $E \in \mathcal{E}$. One can easily compute $p_0(1) = p_0(0)(1 - \lambda Z) + \lambda N$, where $Z = 1 + e^{-\beta\hbar\omega}$, $N = p_0(0) + p_1(0)$ and $\lambda := E_{01}$. By recursion,

$$p_0(n) = p_0(0)(1 - \lambda Z)^n + \frac{N}{Z} (1 - (1 - \lambda Z)^n).$$

We can define $n = t/t_{\text{int}}$, with t_{int} the duration of a single interaction. We will take the limit $t_{\text{int}} \rightarrow 0$, $\lambda \rightarrow 0$, while keeping $Z\lambda/t_{\text{int}} \rightarrow \xi \geq 0$ finite (Z is a constant that we absorbed in the definition of ξ). Then one can check that $(1 - \lambda Z)^n \rightarrow e^{-t/\xi}$ and hence we regain Eq. (7.4). Here $\xi \geq 0$ is a free parameter. So the subsystem decays exponentially to population proportional to the Gibbs distribution (whenever $\xi > 0$).

Alternatively, from the master equation point of view, we can consider Davies maps, which are routinely used as a simple model of a system weakly interacting with a large thermal bath [111], or in the low-density limit [112]. A formal definition is given in [113]:

Definition 7.7. A Davies map $\mathcal{M}$ is a map such that

1. $\mathcal{M} = \exp(\mathcal{L}t)$. Here $\mathcal{L} = \mathcal{H} + \mathcal{L}'$, with $\mathcal{H}(\rho) = [\rho, H]$, H hermitian operator and $\mathcal{L}'$ a general Lindbladian.
2. $[\mathcal{H}, \mathcal{L}'] = 0$ (covariance).
3. $\text{Tr} [\mathcal{L}'(B e^{-\beta H}) A] = \text{Tr} [B \mathcal{L}'(e^{-\beta H} A)]$ for all A, B .

The action of the most general qubit Davies map on a two-level system was studied in [113], Section 3. On the population of two-level systems, one can check by a direct calculation that they induce the evolution of Eq. (7.4).

Now, what is the connection with the resource theory approach? This can be clarified as follows. *Markovian EDPs* are defined here as the subset of EDPs given by embeddable stochastic matrices; i.e. there is some generator L and $t \geq 0$ such that $E = e^{Lt}$ [114]. Then

Proposition 7.8. *Markovian EDPs induce the same evolution (7.4) of collision models and Davies maps on the population of two-level systems.*

Proof. For E to be a valid stochastic matrix, L must satisfy $L_{i|j} \geq 0$ for $i \neq j$ and $\sum_i L_{i|j} = 0$ for all j [115]. Detailed balance is equivalent to $L\mathbf{g} = 0$, that gives $L_{i|j} = e^{-\beta\hbar(\omega_i - \omega_j)} L_{j|i}$. A direct calculation then leads to Eq. (7.4). ■

7.1.5 Elementary Thermal Operations: a sketch

So far we have introduced and motivated a new set of thermodynamic stochastic processes, called Elementary Detailed balanced Processes, as a physically motivated subset of the thermal processes $\mathcal{T}$. To what extent can one go beyond this and define a fully-fledged quantum resource theory? In other words, how do we identify a simple class of quantum operations within the set of Thermal Operations $\mathcal{T}$? In the same spirit of the previous discussion, we may impose a quantum-mechanical analogue of detailed balance. We sketch here some ideas.

Recall that given a stochastic process P with fixed point $\mathbf{g}$, time-reversal is defined as a stochastic process $\overleftarrow{P}$ with transition probabilities satisfying [116]²

$$g_j \overleftarrow{P}_{i|j} = g_i P_{j|i}. \quad (7.5)$$

Detailed balance is then equivalent to time-reversal invariance, $\overleftarrow{P} = P$, as one can readily check substituting $P_{j|i} = g_j / g_i P_{i|j}$ in the previous equation.

This observation allows us to use the definition of time-reversal for a quantum maps to impose quantum detailed balance on thermal maps:

Definition 7.9 (Time-reversal [117]). Given a quantum channel $\mathcal{E}$ with a fixed point γ_S , its time-reversal $\overleftarrow{\mathcal{E}}$ is

$$\overleftarrow{\mathcal{E}}(\rho) := \gamma_S^{1/2} \mathcal{E}(\gamma_S^{-1/2} \rho \gamma_S^{-1/2}) \gamma_S^{1/2}. \quad (7.6)$$

A subset of Thermal Operations of interest is then the set of time-reversal invariant Thermal Operations. Alternatively, going one step further, we can introduce the following quantum generalisation of EDPs:

²This ensures that $g_{i_1} P_{i_2|i_1} \dots P_{i_f|i_{f-1}} = g_{i_f} \overleftarrow{P}_{i_{f-1}|i_f} \dots \overleftarrow{P}_{i_1|i_2}$. $\overleftarrow{P}$ is also a stochastic process and has $\mathbf{g}$ as a fixed point.

Definition 7.10 (Elementary Thermal Operations). An Elementary Thermal Operation $\mathcal{E}$ is a time-reversal invariant Thermal Operation acting only on a qubit subsystem.

One can check that this recovers detailed balance, defined before, as a “zero mode” condition. In fact, consider the matrix elements in the eigenbasis of H_S :

$$c_{m'|n'}^{m|n} = \langle m | \mathcal{E}(|n\rangle\langle n'|) | m' \rangle \quad \overleftarrow{c}_{m'|n'}^{m|n} = \langle m | \overleftarrow{\mathcal{E}}(|n\rangle\langle n'|) | m' \rangle. \quad (7.7)$$

Then,

$$\overleftarrow{c}_{m'|n'}^{m|n} = \begin{cases} e^{-\beta\hbar(\omega_m - \omega_n)} c_{n'|m'}^{n|m} & \text{if } \omega_m - \omega_n = \omega_{m'} - \omega_{n'} = \omega \\ 0 & \text{otherwise.} \end{cases} \quad (7.8)$$

Time-reversal invariance, $\overleftarrow{c}_{m'|n'}^{m|n} = c_{m'|n'}^{m|n}$, leads to a hierarchy of non-trivial conditions on each mode of the map.

The existence of a natural generalisation of the classical discussion given above leads one to question if this alternative definition for a set of thermodynamic transformations admits realisations through simple physical models in the fully quantum case; moreover a natural question is if this thermodynamic model is equivalent to Thermal Operations. The expectation is that this is not the case and that tighter conditions can be found. These issues are currently under investigation.

7.2 Optimal coherence preservation under Markovian covariant processes

Resource theory formulations are based on the notion of state interconversion through quantum channels, whereas a lot of open system dynamics is studied through the lenses of time-evolution under master equations.

Applying resource theory ideas to the study of master equations can: help bridge the language gap with the open systems dynamics community; understand the limitations imposed by a common assumption such as Markovianity on the allowed state interconversions; deepen our understanding of how non-Markovianity affects our ability to preserve asymmetry, and quantum coherence in particular; develop thermodynamic considerations more easily applicable to real-world applications. We give now a quick overview of some of these points, that we are currently investigating.

7.2.1 Covariant Lindbladians

A crucial step in the above considerations is to understand the limits of state transformations under CPTP covariant dynamics that are Markovian.

A map $\mathcal{E}_t$ is defined to be (time-independent) Markovian if $\mathcal{E}_t = e^{\mathcal{L}_H t}$ for some t , where $\mathcal{L}_H$ is a Lindbladian, i.e. the generator of a one-parameter quantum dynamical semi-

group. The general form of $\mathcal{L}_H$ is given by [118, 119]

$$\mathcal{L}_H(\cdot) = \mathcal{A}(\cdot) - \frac{1}{2}\{\mathcal{A}^\dagger(\mathbb{I}), \cdot\}_+ - i[\cdot, H], \quad (7.9)$$

where H is a Hermitian operator, $\mathcal{A}$ is a CP map, $\mathcal{A}^\dagger$ is the adjoint of $\mathcal{A}$ (with respect to the Hilbert-Schmidt inner product, $\text{Tr}[\rho\mathcal{A}(\sigma)] = \text{Tr}[\mathcal{A}^\dagger(\rho)\sigma]$) and $\{\cdot, \cdot\}_+$ denotes the anticommutator.

If $\mathcal{E}_t$ is covariant then $\mathcal{L}_H$ must be covariant, and it has been shown that $\mathcal{A}$ can also be chosen to be covariant [120]. Define $\mathcal{H}(\cdot) = [\cdot, H]$ and $\mathcal{L} = \mathcal{L}_H + i\mathcal{H}$. Since $[\mathcal{L}, \mathcal{H}] = 0$, the evolution induced by $\mathcal{L}_H$ and $\mathcal{L}$ is the same up to an energy-preserving unitary: $\mathcal{E}_t = \mathcal{U}_t \circ e^{\mathcal{L}t}$, $\mathcal{U}_t = e^{-iHt}(\cdot)e^{iHt}$. Hence, from now on, we will ignore the term involving H and consider Lindbladians of the form

$$\mathcal{L}(\cdot) = \mathcal{A}(\cdot) - \frac{1}{2}\{\mathcal{A}^\dagger(\mathbb{I}), \cdot\}_+. \quad (7.10)$$

Since $\mathcal{L}$ is covariant, it acts on each mode independently. The action of $\mathcal{L}$ on the diagonal of a density matrix is therefore completely described by a matrix $\mathcal{L}^{(0)}$ with elements

$$\mathcal{L}_{x'|x}^{(0)} = \langle x' | \mathcal{L}(|x\rangle\langle x|) | x' \rangle := l_{x'|x}. \quad (7.11)$$

The covariant map $\mathcal{E}_t$ acts on the diagonal elements as a stochastic matrix Λ_t , and so $\mathcal{L}^{(0)}$ is the generator of such a matrix. In other words, Λ_t must be an embeddable stochastic matrix [114]: $\Lambda_t = e^{\mathcal{L}^{(0)}t}$. This implies that $l_{x'|x}$ satisfy $l_{x'|x} \geq 0$ for $x' \neq x$ and $\sum_{x'} l_{x'|x} = 0$ [115], which obviously results in $l_{x'|x'} \leq 0$ for all x' . Notice that one can use the condition that Λ_t is an embeddable matrix to specify necessary conditions for $\mathcal{E}_t$ to be Markovian. However, here we will present preliminary results on the effect of Markovianity on coherence evolution.

7.2.2 Optimal coherence preservation under Markovian covariant processes

Given the generator $\mathcal{L}$ of a covariant Markovian process, the elements $l_{x'|x}$ define the diagonal action of the map. We now present a bound on the evolution of coherence that depends only on this classical action. We express a density matrix element as $\rho_{xy} = |\rho_{xy}| \vartheta_{xy}$.

Theorem 7.11. *Let $\mathcal{L}$ be the generator of a covariant Markovian process. Then*

$$\frac{d|\rho_{x'y'}|}{dt} \leq -\gamma_{x'y'} |\rho_{x'y'}| + \sum_{\substack{x \neq x' \\ y \neq y'}}^{(\omega_{x'y'})} \sqrt{l_{x'|x} l_{y'|y}} |\rho_{xy}|, \quad (7.12)$$

where the decay parameter $\gamma_{x'y'} = \frac{1}{2}(|l_{x'|x'}| + |l_{y'|y'}|)$. Furthermore, the bound is attained at all t

when the initial phase-matching condition

$$\vartheta_{x'y'}(0)\vartheta_{xy}^*(0) = \vartheta_{x'x}(0)\vartheta_{y'y}^*(0) \quad (7.13)$$

holds for every $|x\rangle\langle y|$ in the same mode as $|x'\rangle\langle y'|$.

Proof. Here we only sketch a physically motivated derivation of the inequality (a complete proof will be given in a forthcoming work). A Markovian quantum channel $\mathcal{E}_t$ satisfies the semigroup property $\mathcal{E}_{t+dt} = \mathcal{E}_t\mathcal{E}_{dt}$. The idea is to impose the CP condition of Eq. (5.11) at each “infinitesimal” time-step. If we expand Λ_{dt} for short times dt as

$$\Lambda_{dt} = e^{\mathcal{L}^{(0)}dt} = \mathbb{I} + \mathcal{L}^{(0)}dt + o(dt), \quad (7.14)$$

then Eq. (5.11) constrains the evolution of coherences in the following way:

$$|\rho_{x'y'}(t+dt)| \leq \sum_{x,y}^{(\omega_{x'y'})} |\rho_{xy}(t)| \sqrt{[\Lambda_{dt}]_{x'x}[\Lambda_{dt}]_{y'y}}. \quad (7.15)$$

Using Eq. (7.14) we find the matrix elements of Λ_{dt} . The right-hand-side of the previous equation becomes

$$\sum_{x \neq x', y \neq y'}^{(\omega_{x'y'})} |\rho_{xy}(t)| \sqrt{l_{x'|x}l_{y'|y}dt + o(dt)} + |\rho_{x'y'}(t)| \sqrt{(1 + l_{x'|x'}dt + o(dt))(1 + l_{y'|y'}dt + o(dt))}$$

Expanding the expression under the square root, dividing by dt and taking the limit $dt \rightarrow 0$, we obtain Eq. (7.12). The proof that the phase-matching condition allows the bound to be attained requires a more careful analysis. $\blacksquare$

Remark 7.12. For any non-trivial transformation we have matrix elements $l_{x'|x'} \neq 0$, and hence the term involving $\gamma_{x'y'}$ will be strictly positive and induce a decay of $|\rho_{x'y'}|$. In fact, one can prove that for any non-trivial process the solution $\rho_{x'y'} \equiv 0$ is an attractor of the dynamics. Recall from Chapter 5 that under covariant operation perfect shifting of coherence was possible. We see here that Markovian processes cannot achieve this. A simple corollary is that perfect shifting of coherence necessarily requires non-Markovianity to happen.

Remark 7.13. The initial phase-matching condition is always satisfied for pure ρ and for mixed ρ with real phase factors. Moreover, independently of the form of ρ , phase-matching also holds for modes consisting of a single element, which in particular applies to any system with non-degenerate Bohr spectrum. Finally, the phase-matching condition is fulfilled for modes consisting of two off-diagonal elements with a common index, e.g., $|0\rangle\langle 1|$ and $|1\rangle\langle 2|$.

Non-degenerate Bohr spectrum and coherence decay

When the Bohr spectrum is non-degenerate, Eq. (7.12) from Theorem 7.11 simplifies considerably so that each off-diagonal term of the density matrix evolves independently according to

$$\frac{d|\rho_{x'y'}|}{dt} \leq -\gamma_{x'y'}|\rho_{x'y'}|. \quad (7.16)$$

Moreover, as mentioned in Remark 7.13, the initial phase-matching condition within each mode is always satisfied so that the above bound can be saturated. Therefore the solution for optimal coherence preservation yields an exponential decay for every off-diagonal element: $|\rho_{x'y'}(t)| = |\rho_{x'y'}(0)| \exp(-\gamma_{x'y'}t)$. As a particular example, let us consider the simplest case of a qubit and compare with well-known results.

Example 7.14 (Markovian coherence decay on a qubit). For $n \geq 1$, a direct calculation shows that $[\mathcal{L}^{(0)}]^n = \mathcal{L}^{(0)}[l_{0|0} + l_{1|1}]^{n-1}$. Hence, given a generator $\mathcal{L}^{(0)}$, we can easily find the stochastic matrix Λ_t responsible for the evolution of the diagonal elements of a density matrix. By direct inspection one finds that the population reaches equilibrium exponentially with relaxation time $1/T_1 = 2\gamma_{01}$. At the same time, we find that the optimal solution to Eq. (7.16) yields a decoherence time $1/T_2 = \gamma_{01}$. Hence, the well-known relation $2T_1 \geq T_2$ holds. Moreover, preliminary results show a gap between the maximum coherence that can be preserved by a general covariant channel as compared to a Markovian covariant channel, showing that non-Markovianity is a useful resource to coherence preservation.

The constraints above can be specialised to thermodynamics by imposing further conditions on the stochastic map generating the process.

7.3 Equilibration, MaxEnt, Passivity: non-commuting case

A good deal of attention has been devoted lately to the issue of identifying “genuinely quantum mechanical” features in non-macroscopic quantum systems. The most obvious candidates to consider are entanglement in thermodynamics and coherence.

On the other hand, it is unclear to what extent *non-commutativity* impacts thermal resource theories. Indeed, at first glance considerations on conserved quantities might seem to prohibit the inclusion of non-commutativity into this setting. However, one can simply have non-commutativity among *multiple* conserved charges (e.g. quantities entering the generalised Gibbs ensemble in integrable systems [121]). We now shall generalise the concept of resource theory based on a conservation law to the non-commuting case.

7.3.1 Resource theories and non-commuting conservation laws

For simplicity, we define here a resource theory with two non-commuting conserved quantities, the generalisation to more charges being obvious. A (H, A, B) -conserving the-

ory is defined as

$$\mathcal{E}(\rho) = \text{Tr}_B \left[U(\rho \otimes \gamma_B) U^\dagger \right], \quad (7.17)$$

where γ_B is any free state in some set of generalized bath states, and $[U, H_{\text{tot}}] = [U, A_{\text{tot}}] = [U, B_{\text{tot}}] = 0$. Here A_{tot} and B_{tot} denote the sum of the charge observables on the primary system and their corresponding observables on the generalized bath system, $A_{\text{tot}} = A + A_B$, and similarly for B . We are in particular interested in the case where $[A, B] \neq 0$.

Researchers in the quantum information community have already considered information-theoretic aspects of spin baths in thermodynamics, for example [122]. However, here we would like to address two different questions:

1. What constraints are imposed on the free bath states in the case of conserved non-commuting charges?
2. Is there concordance between the maximum entropy principle, resource formulations, and the notion of dynamical equilibration in the presence of non-commuting charges?

The answer to the first question in the commuting case is that non-trivial thermodynamic processes reduce the free states to be of Gibbsian form (canonical or grand-canonical for example) and that other approaches – modulo some caveats – agree with this. We now reconsider these questions in the non-commuting scenario.

7.3.2 Disagreement between different perspectives on free states

Max entropy principle

The *maximum entropy constructions work equally well for commuting or non-commuting observables*. Given constraints on the expectations of quantum observables $\{Q_1, Q_2, \dots\}$, the maximum entropy state is again unique, and of the same Gibbsian form $\rho_\star \propto \exp[-\lambda_1 Q_1 - \lambda_2 Q_2 \dots]$. It therefore takes the same functional form as the bath states for the canonical and grand canonical scenarios. Given that the Gibbsian form arises under maximum entropy constructions, one can ask whether it is possible to have concordance with other arguments leading to the canonical state in the commuting case. Here we briefly analyse dynamical equilibration and complete passivity in the non-commuting regime.

Dynamical account

The case of a set of multiple conserved charges $\mathcal{Q} = \{Q_1, Q_2, \dots\}$, some of which are non-commuting, turns out to have non-trivial features. For simplicity we consider the example of $\mathcal{Q} = \{X, Y\}$, where X and Y are Pauli operators in an effective qubit subsystem, since it captures the essential ingredients of the more general case. Aside from the energy spectrum constraints (which are independent due to commutativity), the maximum entropy state on this effective qubit subsystem takes the form $\rho_\star \propto \exp[-\lambda_1 X - \lambda_2 Y]$, under

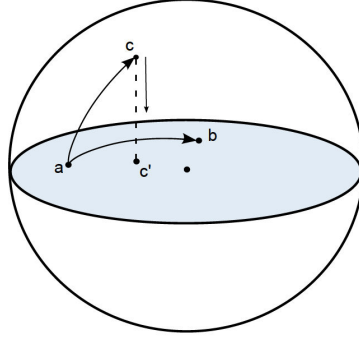


Figure 7.3. Non-commuting bath degrees of freedom. The shaded disk is set of maximum entropy states $\propto \exp[-\lambda_1 X - \lambda_2 Y]$, parametrised by (λ_1, λ_2) , for the conserved quantities Pauli X and Pauli Y of a qubit degree of freedom (here $H \propto \mathbb{I}$). The transformations $a \rightarrow b$ and $a \rightarrow c$ are both unitary, but the former corresponds to a reversible change of external parameters that keeps the state in the shaded disk, while the latter moves off the Gibbs manifold. The maximum entropy projection to the state $c' = \pi(c)$ does not correspond to a physically realisable equilibration process. The maximum entropy state can be written in a frame independent form $\exp[-\lambda \cdot \sigma]/Z$, where $\lambda = (\lambda_1, \lambda_2, 0)$ denotes a particular physically defined axis of the problem. The case λ has at most one non zero element corresponds to the case where there is direct agreement between the three equilibrium perspectives. Otherwise, further considerations must be taken into account.

constraints on the expectation values of X and Y (with λ_1, λ_2 functions of $\langle X \rangle, \langle Y \rangle$, respectively). A dynamical account of equilibration would involve a non-equilibrium state, subject to these constraints, that evolves under some dynamics to ρ_* (see Fig. 7.3).

Such an equilibration process cannot coincide with the maximum entropy construction. The reason is that for this particular model, such a map $\mathcal{E}$ turns out to be a positive, but not *completely positive* quantum map, in the sense that if applied to a subsystem of an maximally entangled state it generates negative probabilities.³ Therefore, such equilibration to the maximum entropy state ρ_* cannot occur exactly as described.⁴

Resource theory account

One also obtains subtleties when we consider the complete passivity construction of free resource states for non-commuting conserved charges. The conservation law requires consistent constraints on the free bath states, in the sense that the degrees of freedom one wishes to consider should not be trivialised. It turns out for a non-commuting case that this problem can be viewed in a number of ways.

We can begin by considering the scenario where one wishes to define a bath state ρ_* to be (A, B) -completely passive, in the sense that given many copies of the state, we

³This is seen by computing $\tilde{\rho} = \mathcal{E} \otimes id(|\Omega\rangle\langle\Omega|)$ on the pure bipartite, maximally entangled state given by $|\Omega\rangle = (|00\rangle + |11\rangle)/\sqrt{2}$. Since $|\Omega\rangle\langle\Omega|$ can be written as $\frac{1}{4}(\mathbb{I} + XX)(\mathbb{I} + ZZ) = \frac{1}{4}(\mathbb{I} + XX + ZZ - YY)$, one finds that $\tilde{\rho} = \frac{1}{4}(\mathbb{I} + XX - YY)$ which has eigenvalues $\{\frac{3}{4}, \frac{1}{4}, \frac{1}{4}, -\frac{1}{4}\}$, and therefore does not correspond to a physically allowed quantum state on the global system.

⁴Note that a similar situation may arise even for multipartite systems with local observables, due to the fact that equilibration requires a complete decorrelation, that may not be a completely positive map [123]. We leave this as an interesting open question.

cannot increase the expectation value of either A or B without bound. We now see what constraints are present in the case of $[A, B] \neq 0$. In particular, (A, B) -complete passivity implies that $\rho_\star$ is separately A -passive and B -passive. As already discussed above, this implies $[\rho_\star, A] = [\rho_\star, B] = 0$. However these conditions are satisfied if and only if

$$\rho_\star = \sum_k c_k C_k, \text{ with } c_k \in \mathbb{R}, \quad (7.18)$$

for some collection of observables $C_k \in \text{Com}(A) \cap \text{Com}(B)$, where $\text{Com}(X)$ is the commutant of the operator X . The significance of this is that any (A, B) -passive state *cannot* contain any component of A or B in it. To explain what this means, we again for simplicity consider the case of a trivial Hamiltonian, and where the only operator that commutes with A and B is one proportional to the identity (as in the qubit example introduced before, where $A = X$ and $B = Y$). In this case the only passive or completely-passive state with respect to (A, B) is the maximally mixed state $\mathbb{I}/d$. In particular, it is *impossible* to reproduce the maximum entropy Gibbsian distribution in the A and B degrees of freedom. This is not to say that a resource theory is impossible; instead the bath states act as random noise in the non-commuting charge degrees of freedom, causing a disconnection with the maximum entropy principle.

We formalize this as a more general statement.

Lemma 7.15. *Let $\mathcal{Q} = \{H, Q_1, Q_2, \dots, Q_n\}$ be a set of conserved charges with H the Hamiltonian for the system. Let $\mathcal{A}(\mathcal{Q})$ denote the algebra generated by $\mathcal{Q}$ and $G(\mathcal{Q})$ denote the symmetry group generated by these charges. If $\rho_\star$ is $\mathcal{Q}$ -passive then $\rho_\star$ must lie in the commutant of $\mathcal{A}(\mathcal{Q})$, and is a symmetric state with respect to $G(\mathcal{Q})$.*

If any of $Q_1, \dots, Q_n$ fail to commute then a strict subset of the Gibbs states are $\mathcal{Q}$ -passive.

We have shown that a disconnection occurs between maximum entropy principles and both the dynamical and complete passivity formulations. In the remaining part of this section we investigate this further and discuss alternative models.

7.3.3 A weaker passivity constraint

The preceding analysis showed that a direct application of passivity notions lead to strong constraints on the A and B degrees of freedom in the free states of the resource theory, which differ from the above maximum entropy state. It is therefore of interest to elaborate further on the link between resource theories and the maximum entropy construction. For the sake of simplicity we illustrate it for the case of the canonical Gibbs state. For a Hamiltonian H it is straightforward to show that one can introduce a notion of free energy via $S(\rho||\gamma) := \beta(F(\rho) - F(\gamma))$, where γ is the Gibbs state with a temperature given by $kT = \beta^{-1}$. Expanding out the left-hand-side, it is immediately found that $F(\rho) = \text{Tr}[H\rho] - \beta^{-1}S(\rho)$ is the relevant free energy function. However, since $S(\rho||\sigma) \geq 0$ with equality if and only if $\rho = \sigma$, we recover the age-old result that the Gibbs state minimizes the free energy. Put another way, the expression for $F(\rho)$ immediately implies

that the Gibbs state must uniquely *maximize* entropy for a fixed energy expectation value $\text{Tr}[H\rho] = \bar{u}$. Moreover, the connection with passivity follows if we consider a unitary transformation that is allowed to change the energy expectation value. From the unitary invariance of the von-Neumann entropy, such unitary gives a change in free energy equal to $\Delta F = \beta(\text{Tr}[HU\rho U^\dagger] - \text{Tr}[H\rho])$; however since the Gibbs state minimizes the free energy, it follows that no unitary (more generally, no constant entropy transformation) can decrease the energy expectation of γ and therefore the state is passive [124]. Moreover, since free energy is an *additive* function, precisely the same argument holds for arbitrarily many copies of $\rho^{\otimes n}$ and thus one deduces complete passivity in the same manner.

For the case of non-commuting charges (and $H \propto \mathbb{I}$ for simplicity) one can turn things around and deduce a weaker condition than in the previous section which, instead of yielding strong constraints on the A - B degrees of freedom, gives a Gibbsian form. Specifically if we consider $S(\rho||\rho_\star)$ where $\rho_\star = \exp[-\lambda_1 A - \lambda_2 B]/Z$, and make use of $S(\rho||\rho_\star) \geq 0$, then we see that the maximum entropy state is only passive in the sense that

$$\lambda_1 \text{Tr}[A\rho] + \lambda_2 \text{Tr}[B\rho] := \text{Tr}[\mathcal{O}(\lambda_1, \lambda_2)\rho] \quad (7.19)$$

cannot be decreased in a constant entropy transformation, such as over the set of all unitaries, for fixed λ_1 and λ_2 . Here the maximum entropy principle is therefore associated to a weaker form of passivity, where a state is only required to be $\mathcal{O}(\lambda_1, \lambda_2)$ -completely passive, instead of (A, B) -completely passive. It is only if $[A, B] = 0$ that this can be further split into *independent* variations in $\langle A \rangle$ and $\langle B \rangle$, and the two approaches coincide.

As a final observation to be subject to further exploration, one can wonder if it is consistent to apply the maximum entropy principle to two non-commuting observables without imposing uncertainty relations among them.

7.3.4 Physical considerations on constrained passivity

Observe that one can interpret λ_1 and λ_2 as either Lagrange multipliers in an extremum problem, or as physical constraint parameters that are defined by the physics. There are good reasons why it may be sensible to frame the problem in this way. For example, one can view λ_1 and λ_2 as local field strengths within our Hamiltonian that couple to these non-commuting observables. Now, it is well-established that the low temperature states of interacting spin systems (such as Ising models with transverse magnetic fields) display thermodynamic phase transitions depending on the particular external field parameters, and are intrinsically quantum-mechanical in origin. We may argue that a resource theory formulation involving non-commuting conserved charges benefits from starting with this weakened form of passivity, computing its properties, and then ascertaining if subsequent variation of the parameters displays discontinuities in these properties. More generally, the weaker form of $\mathcal{O}(\lambda_1, \lambda_2)$ -passivity can be viewed as the original notion applied to a fixed “direction” that is singled out as special.

The consideration of the actual physics of the problem leads to another perspective. If

one has non-commuting conserved charges, then these correspond to physical observables with a non-trivial algebraic structure, for example the algebra of spin observables. An alternative approach to constructing a resource theory using this full structure would be to consider the resultant group G generated by the algebra of the charges as providing the ultimate constraint on the resources and quantum operations allowed. However this coincides with the general theory of asymmetry as developed in recent years [38, 39, 41, 45]. For the case of spin observables the free states are simply states symmetric under the group action $U(g)\rho_*U(g)^\dagger = \rho_*$ for all $g \in SU(2)$. This is consistent with the strong form of passivity in the A - B degrees of freedom, in which the free state was constructed solely from observables in $\text{Com}(A) \cap \text{Com}(B)$ – namely only those observables that are invariant under the group action of G . This perspective also provides insight into the weaker notion of passivity in which one obtains a Gibbsian free state in A and B – one may understand this as a physical breaking of the symmetry group due to a preferred external constraint specified by λ_1 , and λ_2 (see Fig. 7.3). This reduces the full group to a commuting subgroup, $U(1)$.

We again formalize these details as a more general statement that is readily verified.

Lemma 7.16. *Let $\mathcal{Q} = \{H, Q_1, Q_2, \dots, Q_n\}$ be a set of conserved charges with H the Hamiltonian for the system. Let $\boldsymbol{\lambda} = (\lambda_0, \lambda_1, \dots, \lambda_n)$ denote external field parameters that break $G(\mathcal{Q})$ to the abelian subgroup $U(1)$ generated by $Q(\boldsymbol{\lambda}) = \sum_k \lambda_k Q_k$. Then, the generalized Gibbs state $\rho_* = \exp[-\lambda_0 H - \sum_k \lambda_k Q_k]$ is $\mathcal{Q}(\boldsymbol{\lambda})$ -completely passive.*

7.4 Conclusions

It is important, in the quest for quantum thermodynamics, to identify genuinely quantum-mechanical effects that defy classical explanation. Beyond the foundational interest, one reason is that experience with quantum information and computation suggests that these very effects provide advantages over any classical realisation of certain tasks. A quantum information approach to thermodynamics should benefit from the technical framework developed to investigate the gap between classical and quantum computation, especially given the intimate relation between the two subjects that dates back to Maxwell, Szilad, Landauer and Bennett. In this thesis we focused on the study of quantum coherence and how this changes our idea of entropy; we briefly reported ideas about non-commutativity of the theory, another typically quantum-mechanical feature.

However, arguably, current approaches failed to point out operational scenarios where the gap is unequivocal. Among other things, the issue of making “fair” comparisons is hindering developments. A resource theory approach may help to set clear rules of the game and offer a paradigm for such comparisons. But if experience with quantum computation is of any guidance, there are two overarching lessons: first, given an advantage, to point out exactly what quantum-mechanical features are necessary is a tricky business; second, we only know of a couple of “truly quantum” phenomena, i.e. those that

require a radical reformulation of our vision of the world to be explained classically. Most famously we have Bell inequality violations – but the locality condition makes them unnatural to look at in the context of a thermodynamic protocol – and contextuality. The sort of questions one could ask are: given a thermodynamic model T of underlying degrees of freedom C , what thermodynamic phenomena would necessarily imply a violation of, say, non-contextuality of C ?

Despite these difficulties, from a quantum information perspective finding such gaps is perhaps the most important unanswered question in the context of quantum thermodynamics. Finding “thermodynamic Bell inequalities” remains a fascinating issue beyond our current understanding.

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