Quantum Thermodynamics

An introduction to the thermodynamics of quantum information

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Quidquid praecipies, esto brevis.
(Horaz, Ars poetica 335)

Contents

Preface

What is physics? According to standard definitions in encyclopedias *physics is a science that deals with matter and energy and their interactions*[1]. However, as physicists what is it that we actually do? At the most basic level, we formulate predictions for how inanimate objects behave in their natural surroundings. These predictions are based on our expectation that we extrapolate from observations of the *typical behavior*. If typical behavior is universally exhibited by many systems of the same 'family', then this typical behavior is phrased as a *law*.

Take for instance the infamous example of an apple falling from a tree. The same behavior is observed for any kind of fruit and any kind of tree—the fruit 'always' falls from the tree to the ground. Well, actually the same behavior is observed for any object that is let loose above the ground, namely everything will eventually fall towards the ground. It is this observation of *universal falling* that is encoded in the *law of gravity*.

Most theories in physics then seek to understand the nitty-gritty details, for which finer and more accurate observations are essential. Generally, we end up with more and more fine-grained descriptions of nature that are packed into more and more sophisticated laws. For instance, from classical mechanics over quantum mechanics to quantum field theory we obtain an ever more detailed prediction for how smaller and smaller systems behave.

Realizing this typical mindset of physical theories, it does not come as a big surprise that many students have such a hard time wrapping their minds around *thermodynamics*:

> *Thermodynamics is a phenomenological theory to describe the average behavior of heat and work.*

As a phenomenological theory, thermodynamics does not seek to formulate detailed predictions for the microscopic behavior of *some* physical systems, but rather it aims to provide the most universal framework to describe the typical behavior of *all* physical systems.

'Reflections on the motive power of fire'. The origins of thermodynamics trace back to the beginnings of the industrial revolution [6]. For the first time, mankind started developing artificial devices that contained so many moving parts that it became practically impossible to describe their behavior in full detail. Nevertheless, the first devices, steam engines, already proved to be remarkably useful and dramatically increased the effectiveness of productive efforts.

The founding father of thermodynamics is undoubtedly Sadi Carnot. After Napoleon had been exiled, France started importing advanced steam engines from Britain, which made Carnot realize how far France had fallen behind its adversary from across the channel. Quite remarkably, a small number of British engineers, who totally lacked any formal scientific education, had started to collect reliable data about the efficiency of many types of steam engines. However, it was not at all clear whether there was an optimal design and what the highest efficiency would be.

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[1] This and similar definitions can be found, for instance, in Merriam-Webster.

Nicolas Léonard Sadi Carnot:

Everyone knows that heat can produce motion [2].

Carnot had been trained in the latest developments in physics and chemistry, and it was he who recognized that steam engines need to be understood in terms of their energy balance. Thus, optimizing steam engines was not only a matter of improving the expansion and compression of steam, but actually needed an understanding of the relationship between work and heat [2].

Sadly, Carnot's work [2] was largely ignored by the scientific community until the railroad engineer Émile Clapeyron quoted and generalized Carnot's results. Eventually 30 years later, it was Rudolph Clausius, who put Carnot's insight into a solid mathematical framework [3], which is the same mathematical theory that we still use today—thermodynamics.

Thus, thermodynamics is not only unique among the theories in physics with respect to its mindset, but also with respect to its beginnings. No other theory is so intimately connected with someone never holding an academic position—Sadi Carnot. Formulating the original ideas was thus largely motivated by practical questions and not purely by scientific curiosity. This might explain why more than any other theory, thermodynamics is a framework to describe the typical and universal behavior of any physical system.

Richard P Feynman:
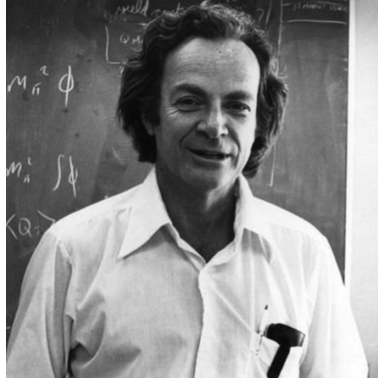
Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy [4].

Quantum computing—Feynman's dream come true. A remarkable quote from Carnot's work [2] is the following:

The study of these engines is of the greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world.

If we replaced the word 'engines' with 'quantum computers', Carnot's sentence would fit nicely into the announcements of the various 'quantum initiatives' around the globe [7].

Ever since Feynman's proposal in the early 1980s [4] quantum computing has been a promise that could initiate a technological revolution. Over the last couple of years big corporations, such as Microsoft, IBM and Google, as well as smaller start-ups, such as D-Wave or Rigetti, have started to present more and more intricate technologies that promise to eventually lead to the development of a practically useful quantum computer.

Rather curiously, we are in a very similar situation to that which Carnot found in the beginning of the 19th century. Novel technologies are being developed by crafty engineers that are much too complicated to be described in full microscopic detail. Nevertheless, the question that we are really after is how to operate these technologies optimally in the sense that the least amount of resources, such as work and information, are wasted into the environment.

As physicists we know exactly which theory will prevail in the attempt to describe what is going on, since it is the only theory that is universal enough to be useful when faced with new challenges—thermodynamics. However, this time the natural variables can no longer be volume, temperature, and pressure, which are

characteristic for steam engines. Rather, in *Quantum Thermodynamics* the first task has to be to identify the new *canonical variables*, and then write the dictionary for how to translate between the universal thermodynamic framework and practically useful statements for the optimization of quantum technologies.

Purpose and target audience of this book. The purpose of this book is to provide a concise introduction to the conceptual building blocks of quantum thermodynamics and their application in the description of quantum systems that process information. Large parts of this book arose from our lecture notes that we had put together for graduate classes in statistical physics or for workshops and summer schools dedicated to quantum thermodynamics. When teaching the various topics of quantum thermodynamics we always felt a bit unsatisfied as no single book contained a comprehensive overview of all the topics we deemed essential. Earlier monographs have become a bit outdated, such as *Quantum Thermodynamics* by our colleagues Gemmer, Michel, and Mahler [5], or are simply not written as a textbook suited for teaching, such as *Thermodynamics in the Quantum Regime* which was edited by Binder *et al* [1].

Thus, we took it upon ourselves to write a text that we will be using for advanced special topics classes in our graduate program. Considering graduate statistical physics and quantum mechanics as prerequisites the topics of the present book can be covered over the course of a semester. However, as always when designing a new course it is simply not possible to cover everything that would be interesting. Thus, we needed to make some tough choices and we hope that our colleagues will forgive us if they feel their work should have been a more prominent part of this text.

Longum iter est per praecepta, breve et efficax per exempla.
(Seneca Junior, 6th letter)

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Acknowledgments

Steve Campbell—I have been fortunate to have enjoyed a menagerie of collaborators over my relatively short research career so far. They all, in their own way, have contributed to how my interests have developed over the years which ultimately led to this work, and for this I am forever grateful. I am particularly indebted to those friends whose work formed the basis for some parts of this book: Marco Genoni, Gian Luca Giorgi, John Goold, Giacomo Guarnieri, Simon Pigeon, Maria Popovic, and Bassano Vacchini. I am also eternally grateful to Tony Apollaro, Barış Çakmak, Gabriele De Chiara, Mossy Fogarty, and Massimo Palma for the many years of stimulating discussions, punctuated with great refreshments, may they long continue.

I am lucky to have gained much of my scientific training from two world-leading physicists, Mauro Paternostro and Thomas Busch. The lessons learned from their expert guidance is woven throughout this book. I feel privileged to have benefitted from their friendship for so many years.

My parents, Larry and Shirley, and brother, Jaymz, I am thankful for all they continue to do for me. Finally, to my loves Flora and Qubit (the cat). Your support and encouragement to undertake and complete this book is the only reason I made it through. For putting up with the life of an early career academic trying to find his place, I owe you everything.

Author biographies

Sebastian Deffner

Dr Sebastian Deffner received his doctorate from the University of Augsburg in 2011 under the supervision of Eric Lutz. From 2011 to 2014 he was a Research Associate in the group of Chris Jarzynski at the University of Maryland, College Park and from 2011 to 2016 he was a Director's Funded Postdoctoral Fellow with Wojciech H Zurek at the Los Alamos National Laboratory. Since 2016 he has been on the faculty of the Department of Physics at the University of Maryland, Baltimore County (UMBC), where he leads the quantum thermodynamics group.

Dr Deffner's contributions to quantum thermodynamics have been recognized through the Early Career Award 2016 from IOP's *New Journal of Physics*, and he was also awarded the Leon Heller Postdoctoral Publication Prize from the Los Alamos National Laboratory in 2016.

To date, Dr Deffner has been reviewing for more than ten international funding agencies and more than thirty high-ranking journals. For these efforts he was named Outstanding Reviewer for *New Journal of Physics* in 2016, Outstanding Reviewer for *Annals of Physics* in 2016, and in 2017 he was named APS Outstanding Referee. Since 2017 Dr Deffner has been a member of the international editorial board for IOP's *Journal of Physics Communications*, and since 2019 he has been on the editorial advisory board of *Journal of Nonequilibrium Thermodynamics*.

As a theoretical physicist, Dr Deffner employs tools from statistical physics, open quantum dynamics, quantum information theory, quantum optics, quantum field theory, condensed matter theory, and optimal control theory to investigate the nonequilibrium properties of nanosystems operating far from thermal equilibrium.

Steve Campbell

After a PhD in Queens University Belfast in 2011 under the supervision of Mauro Paternostro, Dr Steve Campbell moved to University College Cork to work with Thomas Busch in 2012. He spent 2013 at the Okinawa Institute of Science and Technology Graduate University in Japan. Returning to Belfast, he spent 2014 through to 2016 at his *alma mater* Queens University. In 2017 he was awarded a fellowship from the INFN Sezione di Milano and worked with Bassano Vacchini. From February 2019 he has been appointed as Senior Research Fellow at Trinity College Dublin through the award of a Science Foundation Ireland Starting Investigators Research Grant.

Dr Campbell is interested in exploring the role which fundamental bounds, such as the quantum speed limit, play in characterizing and designing thermodynamically efficient control protocols for complex quantum systems. He works on a variety of topics including open quantum systems, critical spin systems and phase transitions, metrology, and coherent control.

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Chapter 1

The principles of modern thermodynamics

Thermodynamics is a phenomenological theory to describe the average behavior of heat and work. Its theoretical framework is built upon five axioms, which are commonly called the *laws of thermodynamics*. Thus, as an axiomatic theory, thermodynamic can never be wrong as long as its basic assumptions are fulfilled.

Despite thermodynamics' unrivaled success, versatility, and universality, it is plagued with three major shortcomings: (i) thermodynamics contains no microscopic information, nor does thermodynamics know how to relate its phenomenological framework to microscopic information; (ii) as an equilibrium theory, thermodynamics cannot characterize nonequilibrium states, and in particular only infinitely slow, quasistatic processes are fully describable; and (iii) as a classical theory the original mathematical framework is ill-equipped to be directly applied to quantum systems.

In the following we will briefly summarize the major building blocks of thermodynamics in section 1.1, and its extension to stochastic thermodynamics in section 1.2. We will then see how equilibrium states can be fully characterized from a quantum information theoretic point of view in section 1.3, which we will use as a motivation to outline the framework of quantum thermodynamics in section 1.4.

1.1 A phenomenological theory of heat and work

Thermodynamics was originally invented to describe and optimize the working principles of steam engines. Therefore, its natural quantities are work and heat. During the operation of such engines, work is understood as the useful part of the energy, whereas heat quantifies the waste into the environment.

In reality, steam engines are messy, stinky, and huge (cf figure 1.1), which makes any attempt to describe their properties from a microscopic theory futile. Thermodynamics takes a very different perspective: rather than trying to understand all the nitty-gritty details, let's focus on the overall, average behavior once the engine is running smoothly—once it has reached its stationary state of operation.

1-1
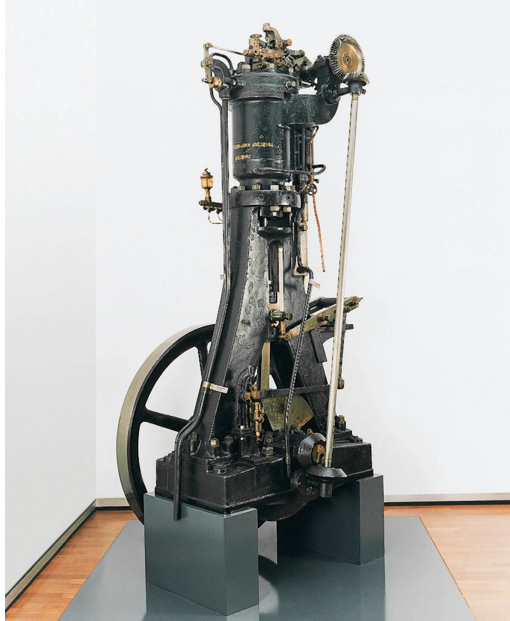
Figure 1.1. Paradigmatic thermodynamic engine: first operational Diesel test engine (M.A.N. museum in Augsburg, Germany).

1.1.1 The five laws of thermodynamics

The framework of thermodynamics is built upon five *laws*, which axiomatically paraphrase ordinary experience and observation of nature. The central notion is *equilibrium*, and the central focus is on transformations of systems from one state of equilibrium to another.

Zeroth law of thermodynamics
The zeroth law of thermodynamics defines a state of *equilibrium* of a system relative to its environment. In its most common formulation it can be expressed as:

> *If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.*

States of equilibrium are uniquely characterized by an *equation of state*, which relates the experimentally accessible parameters. For a steam engine these parameters are naturally given by volume V, pressure P, and temperature T. A sometimes under-appreciated postulate is then that all equilibria can be fully characterized by only *three* accessible parameters, of which only *two* are independent. The equation of state determines how these parameters are related to each other,

$$f(V, P, T) = 0, \tag{1.1}$$
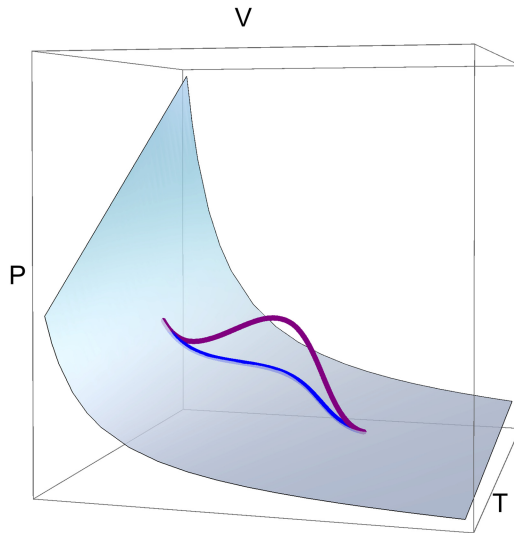
Figure 1.2. Thermodynamic manifold for an ideal gas with $PV = Nk_BT$, and a reversible state transformation (blue) and an irreversible process with the same end points (purple).

where the function f is characteristic for the system. For instance for an ideal gas equation (1.1) becomes the famous $PV = Nk_BT$, where N is the number of particles and k_B is Boltzmann's constant.

Thermodynamic manifolds and reversible processes
Mathematically speaking the equation of state (1.1) defines 2–1 maps, which allow one of the parameters to be written as a function of the other two, $V(P, T)$ or $P(V, T)$ or $T(V, P)$. Except under very special circumstances we regard f as a continuous differentiable function[1]. Thus, the equation of state can be represented as a smooth surface in three-dimensional space.

All equilibrium states for a specific substance are points on this surface. All *thermodynamic transformations* are processes that take the system from one point on the surface to another, cf figure 1.2.

In what follows we will see that only quasistatic processes are fully describable by means of thermodynamics. Quasistatic processes are so slow that the driven systems almost instantaneously relax back to equilibrium. Thus, such processes can be regarded as successions of equilibrium states, which correspond to paths on the surface spanned by the equation of state. Since the surface is smooth, i.e. continuous differentiable, the path cannot have any distinct directionality and this is why we call quasistatic processes that lie entirely in the thermodynamic manifold *reversible*.

All real processes happen in finite time and at finite rates. Such processes necessarily comprise of nonequilibrium states, and paths corresponding to such processes have to leave the thermodynamic surface. Our goal has to be to quantify this irreversibility, which is the starting point of stochastic thermodynamics, see section 1.2

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[1] At loci where f is not continuous differentiable, we have a so-called phase transitions.

Rudolf J E Clausius:

… as I hold it better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call [it] the entropy of the body, from the Greek word 'trope' for 'transformation' I have intentionally formed the word 'entropy' to be as similar as possible to the word 'energy'; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable [4].

First law of thermodynamics

Before we move on to extensions of thermodynamics, however, we need to establish a few more concepts and notions. In classical mechanics the central concept is the energy of the system, since the complete dynamical behavior can be derived from it. We also know from classical mechanics that in isolated systems the energy is conserved, and that transformations of energy can depend on the path taken by the system—think for instance of friction.

This leads naturally to the insight that

$$dE = đW + đQ, \tag{1.2}$$

where E is the internal energy, W the work, and Q denotes the heat. In equation (1.2) work, $đW$, is identified with the contribution to the change in internal energy that can be *controlled*, whereas $đQ$ denotes the amount of energy that is exchanged with a potentially vast bath. Moreover, dE is an exact differential, which means that changes of the internal energy do not depend on which path is taken on the thermodynamic manifold. This makes sense, since we would expect energy to be only dependent on the state of the system, and not how the system has reached a state. In other words, E is a *state function*.

Already in classical mechanics, work is a very different concept. Loosely speaking work is given by a force along a trajectory, which clearly depends on the path a system takes and which explains why $đW$ is a non-exact differential. We can further identify infinitesimal changes in work as

$$đW = -P \, dV, \tag{1.3}$$

which is fully analogous to classical mechanics. The other quantity, the one that quantifies the *useless* change of internal energy, the part that is typically wasted into the environment, the heat Q has no equivalent in classical mechanics. It is rather characterized and specified by the second law of thermodynamics.

Second law of thermodynamics
Let us inspect the first law of thermodynamics as expressed in equation (1.2). If dE is an exact differential, and $đW$ is a non-exact differential, then $đQ$ also has to be non-exact. However, it is relatively simple to understand from its definition how $đW$ can be written in terms of an exact differential. It is the force that depends on the path taken, yet the path length has to be an exact differential—if you walk a closed loop you return to your point of origin with certainty.

Finding the corresponding exact differential, i.e. the line element for $đQ$ was a rather challenging task. A first account goes back to Clausius who realized [4] that

$$\oint \frac{đQ}{T} \leqslant 0 \tag{1.4}$$

where T is the temperature of the substance undergoing the cyclic, thermodynamic transformation. Moreover, the inequality in equation (1.4) becomes an *equality* for quasistatic processes. Thus, it seems natural to define a new state function, S, for reversible processes through

$$dS \equiv \frac{đQ}{T} \tag{1.5}$$

and that is known as *thermodynamic entropy*.

To get a better understanding of this quantity consider a thermodynamic process that takes a system from a point A on the thermodynamic manifold to a point B. Now imagine that the system is taken from A to B along a reversible path, and it returns from B to A along an irreversible path. For such a cycle, the latter two equations give combined,

$$\Delta S_{A \to B} \geqslant \int_A^B \frac{đQ}{T}, \tag{1.6}$$

which is known as the *Clausius inequality*.

The Clausius inequality (1.6) is an expression of the second law of thermo-dynamics. More generally, the second law is a collection of statements that at their core express that the entropy of the Universe is a non-decreasing function of time,

$$\Delta S_{\text{Universe}} \geqslant 0. \tag{1.7}$$

The most prominent, and also the oldest expressions of the second law of thermodynamics are formulated in terms of cyclic processes. The Kelvin–Planck statement asserts that

> *no process is possible whose sole result is the extraction of energy from a heat bath, and the conversion of all that energy into work.*

The Clausius statement reads,

> *no process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature.*

Finally, the Carnot statement declares that

> *no engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs.*

These formulations refer to processes involving the exchange of energy among idealized subsystems: one or more heat reservoirs; a work source—for example, a mass that can be raised or lowered against gravity; and a device that operates in cycles and affects the transfer of energy among the other subsystems. All three statements follow from simple entropy-balance analyses and offer useful, logically transparent reference points as one navigates the application of the laws of thermodynamics to real systems.

Third law of thermodynamics
The third law of thermodynamics, or the Nernst theorem, paraphrases that in *classical* systems the entropy vanishes in the limit of $T \to 0$. A little more precisely, the Nernst theorem states that as absolute zero of the temperature is approached, the entropy change ΔS for a chemical or physical transformation approaches 0,

$$\lim_{T \to 0} \Delta S = 0. \tag{1.8}$$

It is interesting to note that this equation is a modern statement of the theorem. Nernst often used a form that avoided the concept of entropy, since, e.g. for quantum mechanical systems the validity of equation (1.8) is somewhat questionable.

Fourth law of thermodynamics
The fourth law of thermodynamics takes the first step away from a mere equilibrium theory. In reality, few systems can ever be found in isotropic and homogeneous states of equilibrium. Rather, physical properties vary as functions of space $\vec{r}$ and time t.

Nevertheless, it is frequently not such a bad approximation to assume that a thermodynamic system is in a state of *local equilibrium*. This means that for any point in space and time, the system appears to be in equilibrium, yet thermodynamic properties vary weakly on macroscopic scales. In such situations we can introduce the local temperature, $T(\vec{r}, t)$, the local density, $n(\vec{r}, t)$, and the local energy density, $e(\vec{r}, t)$. The question now is, what general and universal statements can be made about the resulting transport driven by local gradients of the thermodynamic variables?

The clearest picture arises if we look at the dynamics of the local entropy, $s(\vec{r}, t)$. We can write

$$\frac{ds}{dt} = \sum_k \frac{\partial s}{\partial X_k} \frac{dX_k}{dt}, \tag{1.9}$$

where $\{X_k\}_k$ is a set of extensive parameters that vary as a function of time. The time-derivative of these X_k define the *thermodynamic fluxes*

$$J_k \equiv \frac{dX_k}{dt} \tag{1.10}$$

and the variation of the entropy as a function of the X_k are the *thermodynamic forces* or *affinities*, F_k. In short, we have

$$\frac{ds}{dt} = \sum_k F_k J_k. \tag{1.11}$$

This means that the rate of entropy production is the sum of products of each flux with its associated affinity.

It should not come as a surprise that equation (1.11) is conceptually interesting, but practically of rather limited applicability. The problem is that generally the fluxes are complicated functions of all forces and local gradients, $J_k(F_0, F_1, \ldots)$. A simplifying case is a purely resistive system, for which by definition the local flux only depends on the instantaneous local affinities. For small affinities, i.e. if the system is in local equilibrium, J_k can be expanded in F_k. In leading order we have,

$$J_k = \sum_j L_{j,k} F_j, \tag{1.12}$$

where the kinetic coefficients $L_{j,k}$ are given by

$$L_{j,k} \equiv \left. \frac{\partial J_k}{\partial F_j} \right|_{F_j=0}, \tag{1.13}$$

with $F_j = 0$ in equilibrium.

The Onsager theorem [39], which is also known as the fourth law of thermodynamics, now states

$$L_{j,k} = L_{k,j}. \tag{1.14}$$

Lars Onsager:

Now if we look at the condition of detailed balancing from the thermodynamic point of view, it is quite analogous to the principle of least dissipation [40].

This means that the matrix of kinetic coefficients is symmetric. Therefore, to a certain degree equation (1.14) is a thermodynamic equivalent of Newton's third law. This analogy becomes even clearer if we interpret equation (1.12) as a thermodynamic equivalent of Newton's second law.

It is interesting to consider when the above considerations break down. Throughout this little exercise we have explicitly assumed that the considered system is in a state of local equilibrium. This is justified as long as the flux and affinities are small. Consider, for instance, a system with a temperature gradient. For small temperature differences the flow is laminar, and the Onsager theorem (1.14) is expected to hold. For large temperature differences the flow becomes turbulent, and the fluxes can no longer be balanced.

1.1.2 Finite-time thermodynamics and endoreversibility

A standard exercise in thermodynamics is to compute the efficiency of cycles, i.e. to determine the relative work output for devices undergoing cyclic transformations on the thermodynamic manifold. However, all standard cycles, such as the Carnot, Otto, Diesel, cycles, etc, have in common that they are comprised of only quasistatic state transformations, and hence their power output is strictly zero.

This insight led Curzon and Ahlborn to ask a slightly different, yet a lot more practical question [7]: 'What is the efficiency of a Carnot engine at maximal power output?' Obviously such a cycle can no longer be reversible, but we still would like to be able to use the methods and notions from thermodynamics. This is possible if one takes the aforementioned idea of *local equilibrium* one step further.

Imagine a device, whose working medium is in thermal equilibrium at temperature T_w, but there is a temperature gradient over its boundaries to the environment

at temperature T. A typical example is a not perfectly insulating thermo-can. Now let us now imagine that the device is slowly driven through a cycle, where slow means that the working medium remains in a local equilibrium state at all instants. However, we will also assume that the cycle operates too fast for the working medium to ever equilibrate with the environment, and thus from the point of view of the environment the device undergoes an irreversible cycle. Such state transformations are called *endoreversible*, which means that locally the transformation is reversible, but globally irreversible.

This idea can then be applied to the Carnot cycle, and we can determine its endoreversible efficiency. The standard Carnot cycle consists of two isothermal processes during which the systems absorbs/exhausts heat and two thermodynamically adiabatic, i.e. isentropic strokes. Since the working medium is not in equilibrium with the environment, we will have to modify the treatment of the isothermal strokes. The adiabatic strokes constitute *no exchange of heat*, and thus they do not need to be re-considered.

During the hot isotherm the working medium is assumed to be a little cooler than the environment. Thus, during the whole stroke the system absorbs the heat

$$Q_h = \kappa_h \tau_h (T_h - T_{hw}), \tag{1.15}$$

where τ_h is the time the isotherm needs to complete and κ_h is a constant depending on thickness and thermal conductivity of the boundary separating working medium and environment. Note that equation (1.15) is nothing else but a discretized version of Fourier's law for heat conduction.

Similarly, during the cold isotherm the system is a little warmer than the cold reservoir. Hence, the exhausted heat becomes

$$Q_c = \kappa_c \tau_c (T_{cw} - T_c) \tag{1.16}$$

where κ_c is the heat transfer coefficient for the cold reservoir.

As mentioned above, the adiabatic strokes are unmodified, but we note that the cycle is taken to be reversible with respect to the *local temperatures* of the working medium. Hence, we can write

$$\Delta S_h = -\Delta S_c \quad \text{and thus} \quad \frac{Q_h}{T_{hw}} = \frac{Q_c}{T_{cw}}. \tag{1.17}$$

The latter will be useful to relate the stroke times τ_h and τ_c to the heat transfer coefficients κ_h and κ_c.

We are now interested in determining the efficiency at maximal power. To this end, we write the power output of the cycle as

$$P(\delta T_h, \delta T_c) = \frac{Q_h - Q_c}{\zeta(\tau_h + \tau_c)} \tag{1.18}$$

where $\delta T_h = T_h - T_{hw}$ and $\delta T_c = T_{cw} - T_c$. In equation (1.18) we introduced the total cycle time $\zeta(\tau_h + \tau_c)$. This means we suppress any explicit dependence of the analysis on the lengths of the adiabatic strokes and exclusively focus on the isotherms, i.e. on

the temperature difference between the working medium and the hot and cold reservoirs.

It is then a simple exercise to find the maximum of $P(\delta T_h, \delta T_c)$ as a function of δT_h and δT_c. After a few lines of algebra one obtains [7]

$$P_{\text{max}} = \frac{\kappa_h \kappa_c}{\zeta} \left(\frac{\sqrt{T_h} - \sqrt{T_c}}{\sqrt{\kappa_h} + \sqrt{\kappa_c}} \right)^2, \tag{1.19}$$

where the maximum is assumed for

$$\frac{\delta T_h}{T_h} = \frac{1 - \sqrt{T_c/T_h}}{1 + \sqrt{\kappa_h/\kappa_c}} \quad \text{and} \quad \frac{\delta T_c}{T_c} = \frac{\sqrt{T_h/T_c} - 1}{1 + \sqrt{\kappa_c/\kappa_h}}. \tag{1.20}$$

From these expressions we can now compute the efficiency. We have,

$$\eta = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{T_{cw}}{T_{hw}} = 1 - \frac{T_c + \delta T_c}{T_h - \delta T_h} \tag{1.21}$$

where we used equation (1.17). Thus, the efficiency of an endoreversible Carnot cycle at maximal power output is given by

$$\eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}}, \tag{1.22}$$

which only depends on the temperatures of the hot and cold reservoirs.

The Curzon–Ahlborn efficiency is one of the first results that illustrate that (i) thermodynamics can be extended to treat nonequilibrium systems, and that (ii) also far from thermal equilibrium universal and mathematically simple relations govern the thermodynamic behavior. In the following we will analyze this observation a little more closely and see how universal statements arise from the nature of fluctuations.

1.2 The advent of Stochastic Thermodynamics

Relatively recently, Evans and co-workers [15] discovered an unexpected symmetry in the simulation of sheared fluids. In small systems the dynamics is governed by thermal fluctuations and, thus, also thermodynamic quantities such as heat and work fluctuate. Remarkably, single fluctuations can be at variance with the macroscopic statements of the second law. For instance, the change of entropy can be negative, or the performed work amounts to less than the free energy difference. Nevertheless, the probability distribution for the thermodynamic observables fulfills a symmetry relation, which has become known as *fluctuation theorem*.

In its most general form the fluctuation theorem relates the probability to find a negative entropy production Σ with the probability of the positive value,

$$\frac{\mathcal{P}(\Sigma = -A)}{\mathcal{P}(\Sigma = A)} = \exp(-A). \tag{1.23}$$

Using Jensen's inequality for exponentials, $\exp(-\langle x\rangle) \geqslant \langle\exp(-x)\rangle$, equation (1.23), immediately implies that

$$\langle\Sigma\rangle \geqslant 0, \qquad (1.24)$$

which is a variation of the Clausius inequality (1.6). Therefore, the fluctuation theorem can be interpreted as a generalization of the second law to systems far from equilibrium. For the average entropy production we retrieve the 'old' statements. However, we also have that negative fluctuations of the entropy production do occur—they are just exponentially unlikely.

The first rigorous proof of the fluctuation theorem was published by Gallavotti and Cohen in 1995 [17], which was quickly generalized to Langevin dynamics [32] and general Markov processes [35].

The discovery of the fluctuation theorems has effectively opened a new area of thermodynamics, which adopted the name *Stochastic Thermodynamics*. Rather than focusing on describing macroscopic systems in equilibrium, stochastic thermo-dynamics is interested in the thermodynamic behavior of small systems that operate far from thermal equilibrium and whose dynamics are governed by fluctuations. Since quantum systems obviously fall into this class, we will briefly summarize the major achievements for classical systems that laid the ground work for what we will eventually be interested in—the thermodynamics of quantum systems.

1.2.1 Microscopic dynamics

To fully understand and appreciate the fluctuation theorem (1.23) we continue by briefly outlining the most important descriptions of random motion. Generally there are two distinct approaches: (i) explicitly modeling the dynamics of a stochastic observable, or (ii) describing the dynamics of the probability density function of a stochastic variable. Among the many variations of these two approaches the conceptually simplest notions are the *Langevin equation* and the *Klein–Kramers equation*.

Langevin equation
In 1908 Paul Langevin, a French physicist, proposed a powerful description of Brownian motion [34, 36]. The Langevin equation is a Newtonian equation of motion for a single Brownian particle driven by a stochastic force modeling the random kicks from the environment,

$$m\ddot{x} + m\gamma\dot{x} + V'(x) = \xi(t). \qquad (1.25)$$

Here, m denotes the mass of the particle, γ is the damping coefficient and $V'(x) = \partial_x V(x)$ is a conservative force from a confining potential. The stochastic force, $\xi(t)$ describes the randomness in a small, but open system due to thermal fluctuations. In the simplest case, $\xi(t)$ is assumed to be Gaussian white noise, which is characterized by,

$$\langle\xi(t)\rangle = 0 \quad \text{and} \quad \langle\xi(t)\,\xi(s)\rangle = 2D\,\delta(t-s), \qquad (1.26)$$

where D is the diffusion coefficient. Despite its apparently simple form, the Langevin equation (1.25) exhibits several mathematical peculiarities. How to properly handle the stochastic force, $\xi(t)$, led to the study of stochastic differential equations, for which we refer to the literature [45].

It is interesting to note that the Langevin equation (1.25) is equivalent to Einstein's treatment of Brownian motion [14]. This can be seen by explicitly deriving the *fluctuation–dissipation theorem* from equation (1.25).

Fluctuation–dissipation theorem
The Langevin equation (1.25) for the case of a free particle, $V(x) = 0$, can be expressed in terms of the velocity $v = \dot{x}$ as,

$$m\dot{v} + m\gamma v = \xi(t). \tag{1.27}$$

The solution of the latter first-order differential equation (1.27) reads,

$$v_t = v_0 \exp(-\gamma t) + \frac{1}{m} \int_0^t ds\, \xi(s) \exp(-\gamma(t - s)), \tag{1.28}$$

where v_0 is the initial velocity. Since the Langevin force is of vanishing mean (1.26), the averaged solution $\langle v_t \rangle$ becomes,

$$\langle v_t \rangle = v_0 \exp(-\gamma t). \tag{1.29}$$

Moreover, we obtain for the mean-square velocity $\langle v_t^2 \rangle$,

$$\begin{aligned}
\langle v_t^2 \rangle = v_0^2 \exp(-2\gamma t) + \frac{1}{m^2} \int_0^t ds_1 \\
\times \int_0^t ds_2 \exp(-\gamma(t - s_1)) \exp(-\gamma(t - s_2)) \langle \xi(s_1)\xi(s_2) \rangle.
\end{aligned} \tag{1.30}$$

With the help of the correlation function (1.26) the twofold integral can be written in closed form and, thus, equation (1.30) becomes,

$$\langle v_t^2 \rangle = v_0^2 \exp(-2\gamma t) + \frac{D}{\gamma m^2}(1 - \exp(-2\gamma t)). \tag{1.31}$$

In the stationary state for $\gamma t \gg 1$, the exponentials become negligible and the mean-square velocity (1.31) further simplifies to,

$$\langle v_t^2 \rangle = \frac{D}{\gamma m^2}. \tag{1.32}$$

However, we also know from kinetic gas theory [2] that in equilibrium $\langle v_t^2 \rangle = 1/\beta m$ where we introduce the inverse temperature, $\beta = 1/k_B T$. Thus, we finally have

$$D = \frac{m\gamma}{\beta}, \tag{1.33}$$

which is the *fluctuation–dissipation theorem*.

Klein–Kramers equation

The Klein–Kramers equation is an equation of motion for distribution functions in position and velocity space, which is equivalent to the Langevin equation (1.25), see also [45]. For a Brownian particle in one dimension it takes the form,

$$\frac{\partial}{\partial t}P(x, v, t) = -\frac{\partial}{\partial x}(vP(x, v, t)) + \frac{\partial}{\partial v}\left(\frac{V'(x)}{m}P(x, v, t) + \gamma vP(x, v, t)\right)$$
$$+ \frac{\gamma}{m\beta}\frac{\partial^2}{\partial v^2}P(x, v, t). \tag{1.34}$$

Note that by construction the stationary solution of the Klein–Kramers equation (1.34) is the Boltzmann–Gibbs distribution, $P_{\mathrm{eq}} \propto \exp(-\beta/2\, mv^2 - \beta V)$. The main advantage of the Klein–Kramers equation (1.34) over the Langevin equation (1.25) is that we can compute the entropy production directly, which we will exploit shortly for quantum systems in section 1.4.5.

1.2.2 Stochastic energetics

An important step towards the discovery of the fluctuation theorems (1.23) was Sekimoto's insight that thermodynamic notions can be generalized to single particle dynamics [46]. To this end, consider the overdamped Langevin equation

$$0 = -(-m\gamma\dot{x} + \xi_t)dx + \partial_x V(x, \lambda)dx, \tag{1.35}$$

where we separated contributions stemming from the interaction with the environment and mechanical forces. Here and in the following, λ is an external control parameter, whose variation drives the system.

Generally, a change in internal energy of a single particle is comprised of changes in kinetic *and* potential energy. In the overdamped limit, however, one assumes that the momentum degrees of freedom equilibrate much faster than any other time-scale of the dynamics. Thus, the kinetic energy is always at its equilibrium value, and thus a change in internal energy, de, for a single trajectory, x, is given by

$$de(x, \lambda) = dV(x, \lambda) = \partial_x V(x, \lambda)dx + \partial_\lambda V(x, \lambda)d\lambda. \tag{1.36}$$

Further, identifying the heat with the external terms in equation (1.35), which are governed by the damping and the noise, we can write

$$dq(x) = (-m\gamma\dot{x} + \xi_t)dx. \tag{1.37}$$

Thus, we obtain a stochastic, microscopic expression of the first law (1.2)

$$0 = -dq(x) + de(x, \lambda) - \partial_\lambda V(x, \lambda)d\lambda, \tag{1.38}$$

which uniquely defines the stochastic work for a single trajectory,

$$dw(x) = \partial_\lambda V(x, \lambda)d\lambda. \tag{1.39}$$

Christopher Jarzynski:

If we shift our focus away from equilibrium states, we find a rich universe of nonequilibrium behavior [29].

Note that the work increment, dw, is given by the partial derivative of the potential with respect to the externally controllable work parameter, λ.

1.2.3 Jarzynski equality and Crooks theorem

The stochastic work increment $dw(x)$ uniquely characterizes the thermodynamics of single Brownian particles. However, since $dw(x)$ is subject to thermal fluctuations none of the traditional statements of the second law can be directly applied and, in particular, there is no maximum work theorem for $dw(x)$. Therefore, special interest has to be on the distribution of $\mathcal{P}(W)$, where $W = \int dw(x)$ is the accumulated work performed during a thermodynamic process.

In the following we will briefly discuss representative derivations of the most prominent fluctuation theorems, namely the classical Jarzynski equality and the Crooks theorem, and then the quantum Jarzynski equality in section 1.4.3 and finally a quantum fluctuation theorem for entropy production in section 1.4.5.

Jarzynski equality
Thermodynamically, the simplest cases are systems that are isolated from their thermal environment. Realistically imagine, for instance, a small system that is *ultraweakly* coupled to the environment. If left alone, the system equilibrates at inverse temperature β for a fixed work parameter, λ. Then, the time scale of the variation of the work parameter is taken to be much shorter than the relaxation time, $1/\gamma$. Hence, the dynamics of the system during the variation of λ can be approximated by Hamilton's equations of motion to high accuracy.

Now, let $\Gamma = (\vec{q}, \vec{p})$ denote a *microstate* of the system, which is a point in the many-dimensional phase space including all relevant coordinates to specify the microscopic configurations $\vec{q}$ and momenta $\vec{p}$. Further, $H(\Gamma; \lambda)$ denotes the Hamiltonian of the system and the Klein–Kramers equation (1.34) reduces for $\gamma \ll 1$ to the Liouville equation,

$$\frac{\partial}{\partial t} P(\Gamma, t) = -\{P(\Gamma, t), H(\Gamma; \lambda)\}, \tag{1.40}$$

where $\{\cdot, \cdot\}$ denotes the Poisson bracket.

We now assume that the system was initially prepared in a Boltzmann–Gibbs equilibrium state

$$p_\lambda^{\mathrm{eq}}(\Gamma) = \frac{1}{Z_\lambda} \exp(-\beta H(\Gamma; \lambda)), \tag{1.41}$$

with partition function Z_λ and Helmholtz free energy, F_λ,

$$Z_\lambda = \int d\Gamma \exp(-\beta H(\Gamma; \lambda)) \quad \text{and} \quad \beta F_\lambda = -\ln Z_\lambda. \tag{1.42}$$

As the system is isolated during the thermodynamic process we can identify the work performed during a single realization with the change in the Hamiltonian,

$$W = H(\Gamma_\tau(\Gamma_0); \lambda_\tau) - H(\Gamma_0; \lambda_0), \tag{1.43}$$

where $\Gamma_\tau(\Gamma_0)$ is a time-evolved point in phase space given that the system started at Γ_0.

It is then a simple exercise to derive the Jarzynski equality for Hamiltonian dynamics [26]. To this end, consider

$$\begin{aligned} \langle \exp(-\beta W) \rangle &= \int d\Gamma_0 \, p_{\lambda_0}^{\mathrm{eq}}(\Gamma_0) \exp(-\beta W(\Gamma_0)) \\ &= \frac{1}{Z_{\lambda_0}} \int d\Gamma_0 \exp(-\beta H(\Gamma_\tau(\Gamma_0); \lambda_\tau)) \\ &= \frac{1}{Z_{\lambda_0}} \int d\Gamma_\tau \left| \frac{\partial \Gamma_\tau}{\partial \Gamma_0} \right|^{-1} \exp(-\beta H(\Gamma_\tau; \lambda_\tau)). \end{aligned} \tag{1.44}$$

Changing variables and using Liouville's theorem, which ensures conservation of phase space volume, i.e. $|\partial\Gamma_\tau/\partial\Gamma_0|^{-1} = 1$, we arrive at,

$$\langle \exp(-\beta W) \rangle = \frac{1}{Z_{\lambda_0}} \int d\Gamma_\tau \exp(-\beta H(\Gamma_\tau; \lambda_\tau)) = \frac{Z_{\lambda_\tau}}{Z_{\lambda_0}} = \exp(-\beta \Delta F). \tag{1.45}$$

The Jarzynski equality (1.45) is one of the most important building blocks of modern thermodynamics [41]. It can be rightly understood as a generalization of the second law of thermodynamics to systems far from equilibrium, and it has been shown to hold in a wide range of classical systems, with weak and strong coupling, with slow and fast dynamics, with Markovian and non-Markovian noise etc [28].

Crooks's fluctuation theorem

The second most prominent fluctuation theorem is the work relation by Crooks [5, 6]. As before we are interested in the evolution of a thermodynamic system for times $0 \leqslant t \leqslant \tau$, during which the work parameter, λ_t, is varied according to some protocol. For the present purposes, we now assume that the thermodynamic process is described as a sequence, $\Gamma_0, \Gamma_1, \ldots, \Gamma_N$, of microstates visited at times $t_0, t_1, \ldots, t_N$ as the system evolves. For the sake of simplicity we assume the time sequence to be equally distributed, $t_n = n\tau/N$, and, implicitly, $(\Gamma_N; t_N) = (\Gamma_\tau; \tau)$. Moreover, we assume that the evolution is a *Markov process*: given the microstate Γ_n at time t_n, the subsequent microstate Γ_{n+1} is sampled randomly from a transition probability distribution, P, that depends merely on Γ_n, but not on the microstates visited at earlier times than t_n [54]. This means that the transition probability to go from Γ_n to Γ_{n+1} depends only on the current microstate, Γ_n, and the current value of the work parameter, λ_n. Finally, we assume that the system fulfills a local detailed balance condition [54], namely

$$\frac{P(\Gamma \to \Gamma'; \lambda)}{P(\Gamma \leftarrow \Gamma'; \lambda)} = \frac{\exp(-\beta H(\Gamma'; \lambda))}{\exp(-\beta H(\Gamma; \lambda))}. \tag{1.46}$$

When the work parameter, λ, is varied in discrete time steps from λ_0 to $\lambda_N = \lambda_\tau$, the evolution of the system during one time step can be expressed as a sequence,

$$\text{forward:} \qquad (\Gamma_n, \lambda_n) \to (\Gamma_n, \lambda_{n+1}) \to (\Gamma_{n+1}, \lambda_{n+1}). \tag{1.47}$$

In this sequence first the value of the work parameter is updated and, then, a random step is taken by the system. A trajectory of the whole process between initial, Γ_0, and final microstate, Γ_τ, is generated by first sampling Γ_0 from the initial, Boltzmann–Gibbs distribution $p_{\lambda_0}^{\text{eq}}$ and, then, repeating equation (1.47) in time increments, $\delta t = \tau/N$.

Consequently, the net change in internal energy, $\Delta E = H(\Gamma_N, \lambda_N) - H(\Gamma_0, \lambda_0)$, can be written as a sum of two contributions. First, the changes in energy due to variations of the work parameter,

$$W = \sum_{n=0}^{N-1} [H(\Gamma_n; \lambda_{n+1}) - H(\Gamma_n; \lambda_n)], \tag{1.48}$$

and second, changes due to transitions between microstates in phase space,

$$Q = \sum_{n=0}^{N-1} [H(\Gamma_{n+1}; \lambda_{n+1}) - H(\Gamma_n; \lambda_{n+1})]. \tag{1.49}$$

As argued by Crooks [5] the first contribution (1.48) is given by an *internal* change in energy and the second term (1.49) stems from the interaction with the environment introducing the random steps in phase space. Thus, equation (1.48) is a natural definition of stochastic work, and equation (1.49) is the stochastic heat for a single trajectory.

The probability to generate a trajectory, $\Xi = (\Gamma_0 \rightarrow \dots \Gamma_N)$, starting in a particular initial state, Γ_0, is given by the product of the initial distribution and all subsequent transition probabilities,

$$P^F[\Xi] = p_{\lambda_0}^{\text{eq}}(\Gamma_0) \prod_{n=0}^{N-1} P(\Gamma_n \rightarrow \Gamma_{n+1}; \lambda_{n+1}), \qquad (1.50)$$

where the stochastic independence of the single steps is guaranteed by the Markov assumption.

Analogously to the *forward* process, we can define a *reverse* trajectory with $(\lambda_0 \leftarrow \lambda_\tau)$. However, the starting point is sampled from $p_{\lambda_\tau}^{\text{eq}}$ and the system first takes a random step and, then, the value of the work parameter is updated,

$$\text{reversed:} \qquad (\Gamma_{n+1}, \lambda_{n+1}) \leftarrow (\Gamma_{n+1}, \lambda_n) \leftarrow (\Gamma_n, \lambda_n). \qquad (1.51)$$

Now, we compare the probability of a trajectory Ξ during a forward process, $P^F[\Xi]$, with the probability of the *conjugated* path, $\Xi^\dagger = (\Gamma_0 \leftarrow \dots \Gamma_N)$, during the reversed process, $P^R[\Xi^\dagger]$. The ratio of these probabilities reads,

$$\frac{P^F[\Xi]}{P^R[\Xi^\dagger]} = \frac{p_{\lambda_0}^{\text{eq}}(\Gamma_0) \displaystyle\prod_{n=0}^{N-1} P\left(\Gamma_n \rightarrow \Gamma_{n+1}; \lambda_{n+1}^F\right)}{p_{\lambda_1}^{\text{eq}}(\Gamma_N) \displaystyle\prod_{n=0}^{N-1} P\left(\Gamma_n \leftarrow \Gamma_{n+1}; \lambda_{N-1-n}^R\right)}. \qquad (1.52)$$

Here, $\{\lambda_0^F, \lambda_1^F, \dots, \lambda_N^F\}$ is the protocol for varying the external work parameter from λ_0 to λ_τ during the forward process. Analogously, $\{\lambda_0^R, \lambda_1^R, \dots, \lambda_N^R\}$ specifies the reversed process, which is related to the forward process by,

$$\lambda_n^R = \lambda_{N-n}^F. \qquad (1.53)$$

Hence, every factor $P(\Gamma \rightarrow \Gamma'; \lambda)$ in the numerator of the ratio (1.52) is matched by $P(\Gamma \leftarrow \Gamma'; \lambda)$ in the denominator.

In conclusion, equation (1.52) reduces to [5],

$$\frac{P^F[\Xi]}{P^R[\Xi^\dagger]} = \exp\left(\beta\left(W^F[\Xi] - \Delta F\right)\right), \qquad (1.54)$$

where $W^F[\Xi]$ is the work performed on the system during the forward process.

Forward work, $W^F[\Xi]$, and reverse work, $W^R[\Xi^\dagger]$, are related through

$$W^F[\Xi] = -W^R[\Xi^\dagger] \qquad (1.55)$$

for a conjugate pair of trajectories, Ξ and $\Xi^\dagger$. The corresponding work distributions, $\mathcal{P}_F$ and $\mathcal{P}_R$, are then given by an average over all possible realizations, i.e. all discrete trajectories of the process,

$$\mathcal{P}_F(+W) = \int d\Xi \, P^F[\Xi] \, \delta\left(W - W^F[\Xi]\right)$$

$$\mathcal{P}_R(-W) = \int d\Xi \, P^R[\Xi^\dagger] \, \delta\left(W + W^R[\Xi^\dagger]\right), \qquad (1.56)$$

where $d\Xi = d\Xi^\dagger = \prod_n d\Gamma_n$. Collecting equations (1.54) and (1.56) the work distribution for the forward processes can be written as

$$\mathcal{P}_F(+W) = \exp(\beta(W - \Delta F)) \int d\Xi \, P^R[\Xi^\dagger] \, \delta(W + W^R[\Xi^\dagger]), \qquad (1.57)$$

from which we obtain the Crooks fluctuation theorem [6]

$$\mathcal{P}_R(-W) = \exp(-\beta(W - \Delta F)) \, \mathcal{P}_F(+W). \qquad (1.58)$$

It is interesting to note that the Crooks theorem (1.58) is a detailed version of the Jarzynski equality (1.45), which follows from integrating equation (1.58) over the forward work distribution,

$$\begin{aligned}
1 &= \int dW \, \mathcal{P}_R(-W) = \int dW \, \exp(-\beta(W - \Delta F)) \, \mathcal{P}_F(+W) \\
&= \langle \exp(-\beta(W - \Delta F)) \rangle_F.
\end{aligned} \qquad (1.59)$$

Note, however, that the Crooks theorem (1.58) is only valid for Markovian processes [27], whereas the Jarzynski equality can also be shown to hold for non-Markovian dynamics [48].

1.3 Foundations of statistical physics from quantum entanglement

In the preceding section we implicitly assumed that there is a well-established theory if and how physical systems are described in a state of thermal equilibrium. For instance, in the treatment of the Jarzynski equality (1.45) and the Crooks fluctuation theorem (1.58) we assumed that the system is initially prepared in a Boltzmann–Gibbs distribution. In standard textbooks of statistical physics this description of canonical thermal equilibria is usually derived from the fundamental postulate, Boltzmann's H-theorem, the ergodic hypothesis, or the maximization of the statistical entropy in equilibrium [2, 52]. However, none of these concepts are particularly well-phrased for quantum systems.

It is important to realize that statistical physics was developed in the XIX century, when the fundamental physical theory was classical mechanics. Statistical physics was then developed to translate between microstates (points in phase space) and thermodynamic macrostates (given by temperature, entropy, pressure, etc). Since microstates and macrostates are very different notions, a new theory became necessary that allows one to 'translate' with the help of fictitious, but useful, concepts such as ensembles. However, ensembles consisting of infinitely many copies of the same system seem rather ill-defined from the point of view of a fully quantum theory.

Only relatively recently this conceptual problem was repaired by showing that the famous representations of microcanonical and canonical equilibria can be obtained from a fully quantum treatment—from symmetry considerations of entanglement [12]. This novel approach to the foundations of statistical mechanics relies on *entanglement assisted invariance* or in short on *envariance* [59–61].

In the following we summarize the main conceptual steps that were originally published in reference [12].

1.3.1 Entanglement assisted invariance

Consider a quantum system, $\mathcal{S}$, which is maximally entangled with an environment, $\mathcal{E}$, and let $|\psi_{\mathcal{SE}}\rangle$ denote the composite state in $\mathcal{S} \otimes \mathcal{E}$. Then $|\psi_{\mathcal{SE}}\rangle$ is called *envariant* under a unitary map $U_{\mathcal{S}} = u_{\mathcal{S}} \otimes \mathbb{1}_{\mathcal{E}}$ if and only if there exists another unitary $U_{\mathcal{E}} = \mathbb{1}_{\mathcal{S}} \otimes u_{\mathcal{E}}$ such that,

$$
\begin{aligned}
U_{\mathcal{S}}|\psi_{\mathcal{SE}}\rangle &= (u_{\mathcal{S}} \otimes \mathbb{1}_{\mathcal{E}})|\psi_{\mathcal{SE}}\rangle = |\eta_{\mathcal{SE}}\rangle \\
U_{\mathcal{E}}|\eta_{\mathcal{SE}}\rangle &= (\mathbb{1}_{\mathcal{S}} \otimes u_{\mathcal{E}})|\eta_{\mathcal{SE}}\rangle = |\psi_{\mathcal{SE}}\rangle.
\end{aligned}
\tag{1.60}
$$

Thus, $U_{\mathcal{E}}$ that does not act on $\mathcal{S}$ 'does the job' of the inverse map of $U_{\mathcal{S}}$ on $\mathcal{S}$—assisted by the environment $\mathcal{E}$.

The principle is most easily illustrated with a simple example. Suppose $\mathcal{S}$ and $\mathcal{E}$ are each given by two-level systems, where $\{|\uparrow\rangle_{\mathcal{S}}, |\downarrow\rangle_{\mathcal{S}}\}$ are the eigenstates of $\mathcal{S}$ and $\{|\uparrow\rangle_{\mathcal{E}}, |\downarrow\rangle_{\mathcal{E}}\}$ span $\mathcal{E}$. Now, further assume $|\psi_{\mathcal{SE}}\rangle \propto |\uparrow\rangle_{\mathcal{S}} \otimes |\uparrow\rangle_{\mathcal{E}} + |\downarrow\rangle_{\mathcal{S}} \otimes |\downarrow\rangle_{\mathcal{E}}$ and $U_{\mathcal{S}}$ is a *swap* in $\mathcal{S}$—it 'flips' its spin. Then, we have

$$
|\uparrow\rangle_{\mathcal{S}} \otimes |\uparrow\rangle_{\mathcal{E}} + |\downarrow\rangle_{\mathcal{S}} \otimes |\downarrow\rangle_{\mathcal{E}} \xrightarrow{U_{\mathcal{S}}} |\downarrow\rangle_{\mathcal{S}} \otimes |\uparrow\rangle_{\mathcal{E}} + |\uparrow\rangle_{\mathcal{S}} \otimes |\downarrow\rangle_{\mathcal{E}}.
\tag{1.61}
$$

The action of $U_{\mathcal{S}}$ on $|\psi\rangle_{\mathcal{SE}}$ can be restored by a swap, $U_{\mathcal{E}}$, on $\mathcal{E}$,

$$
|\downarrow\rangle_{\mathcal{S}} \otimes |\uparrow\rangle_{\mathcal{E}} + |\uparrow\rangle_{\mathcal{S}} \otimes |\downarrow\rangle_{\mathcal{E}} \xrightarrow{U_{\mathcal{E}}} |\downarrow\rangle_{\mathcal{S}} \otimes |\downarrow\rangle_{\mathcal{E}} + |\uparrow\rangle_{\mathcal{S}} \otimes |\uparrow\rangle_{\mathcal{E}}.
\tag{1.62}
$$

Thus, the swap $U_{\mathcal{E}}$ on $\mathcal{E}$ restores the pre-swap $|\psi\rangle_{\mathcal{SE}}$ without 'touching' $\mathcal{S}$, i.e. the global state is restored by solely acting on $\mathcal{E}$. Consequently, local probabilities of the two swapped spin states are both exchanged and unchanged. Hence, they have to be equal. This provides the fundamental connection of quantum states and probabilities [59], and leads to Born's rule [60].

Recent experiments in quantum optics [23, 56] and on IBM's Q Experience [9] have shown that envariance is not only a theoretical concept, but a physical reality. Thus, envariance is a valid and purely quantum mechanical concept that we can use as a stepping stone to *motivate* and *derive* quantum representations of thermodynamic equilibrium states.

1.3.2 Microcanonical state from envariance

We begin by considering the microcanonical equilibrium. Generally, thermodynamic equilibrium states are characterized by extrema of physical properties, such as maximal phase space volume, maximal thermodynamic entropy, or maximal randomness [53]. We will define the microcanonical equilibrium as the quantum

state that is 'maximally envariant', i.e. envariant under all unitary operations on $\mathcal{S}$. To this end, we write the composite state $|\psi_{\mathcal{SE}}\rangle$ in Schmidt decomposition [38],

$$|\psi_{\mathcal{SE}}\rangle = \sum_k a_k |s_k\rangle \otimes |\varepsilon_k\rangle, \tag{1.63}$$

where by definition $\{|s_k\rangle\}$ and $\{|\varepsilon_k\rangle\}$ are orthocomplete in $\mathcal{S}$ and $\mathcal{E}$, respectively. The task is now to identify the 'special' state that is maximally envariant.

It has been shown [60] that $|\psi_{\mathcal{SE}}\rangle$ is envariant under all unitary operations if and only if the Schmidt decomposition is even, i.e. all coefficients have the same absolute value, $|a_k| = |a_l|$ for all l and k. We then can write,

$$|\psi_{\mathcal{SE}}\rangle \propto \sum_k \exp(i\phi_k)|s_k\rangle \otimes |\varepsilon_k\rangle, \tag{1.64}$$

where ϕ_k are phases. Recall that in classical statistical mechanics equilibrium ensembles are identified as the states with the largest corresponding volume in phase space [53]. In the present context this 'identification' readily translates into an equilibrium state that is envariant under the maximal number of, i.e. *all* unitary operations.

To conclude the derivation we note that the microcanonical state is commonly identified as the state that is also fully energetically degenerate [2]. To this end, denote the Hamiltonian of the composite system by

$$H_{\mathcal{SE}} = H \otimes \mathbb{1}_{\mathcal{E}} + \mathbb{1}_{\mathcal{S}} \otimes H_{\mathcal{E}}. \tag{1.65}$$

Then, the internal energy of $\mathcal{S}$ is given by the quantum mechanical average

$$E = \langle \psi_{\mathcal{SE}} | (H \otimes \mathbb{1}_{\mathcal{E}}) | \psi_{\mathcal{SE}} \rangle = \sum_k \langle s_k | H | s_k \rangle / Z_{\text{mic}}, \tag{1.66}$$

where Z_{mic} is the energy-dependent dimension of the Hilbert space of $\mathcal{S}$, which is commonly also called the microcanonical partition function [2]. Since $|\psi_{\mathcal{SE}}\rangle$ (1.66) is envariant under all unitary maps we can assume without loss of generality that $\{s_k\}_{k=1}^{Z_{\text{mic}}}$ is a representation of the energy eigenbasis corresponding to H, and we have $\langle s_k | H | s_k \rangle = e_k$ with $E = e_k = e_{k'}$ for all $k, k' \in \{1, \ldots, Z_{\text{mic}}\}$.

Therefore, we have identified the fully quantum mechanical representation of the microcanonical state by two conditions. Note that in our framework the microcanonical equilibrium is not represented by a unique state, but rather by an equivalence class of all maximally envariant states with the same energy: the state representing the microcanonical equilibrium of a system $\mathcal{S}$ with Hamiltonian H is the state that is (i) envariant under all unitary operations on $\mathcal{S}$ and (ii) fully energetically degenerate with respect to H.

Reformulation of the fundamental statement
Before we continue to rebuild the foundations of statistical mechanics using envariance, let us briefly summarize and highlight what we have achieved so far. All standard treatments of the microcanonical state relied on notions such as

probability, ergodicity, ensemble, randomness, indifference, etc. However, in the context of (quantum) statistical physics none of these expressions are fully well-defined. Indeed, in the early days of statistical physics seminal researchers such as Maxwell and Boltzmann struggled with the conceptual difficulties [53]. Modern interpretation and understanding of statistical mechanics, however, was invented by Gibbs, who simply ignored such foundational issues and made full use of the concept of probability.

In contrast, in this approach we only need a quantum symmetry induced by entanglement—envariance—instead of relying on mathematically ambiguous concepts. Thus, we can reformulate the fundamental statement of statistical mechanics in quantum physics:

The microcanonical equilibrium of a system $\mathcal{S}$ with Hamiltonian H is a fully energetically degenerate quantum state envariant under all unitaries.

We will further illustrate this fully quantum mechanical approach to the foundations of statistical mechanics by also treating the canonical equilibrium.

1.3.3 Canonical state from quantum envariance

Let us now imagine that we can separate the total system $\mathcal{S}$ into a smaller subsystem of interest $\mathfrak{S}$ and its complement, which we call heat bath $\mathfrak{B}$. The Hamiltonian of $\mathcal{S}$ can then be written as

$$H = H_{\mathfrak{S}} \otimes \mathbb{I}_{\mathfrak{B}} + \mathbb{I}_{\mathfrak{S}} \otimes H_{\mathfrak{B}} + h_{\mathfrak{S},\mathfrak{B}}, \tag{1.67}$$

where $h_{\mathfrak{S},\mathfrak{B}}$ denotes an interaction term. Physically this term is necessary to facilitate exchange of energy between the $\mathfrak{S}$ and the heat bath $\mathfrak{B}$. In the following, however, we will assume that $h_{\mathfrak{S},\mathfrak{B}}$ is sufficiently small so that we can neglect its contribution to the total energy, $E = E_{\mathfrak{S}} + E_{\mathfrak{B}}$, and its effect on the composite equilibrium state $|\psi_{\mathcal{SE}}\rangle$. These assumptions are in complete analogy to the ones of classical statistical mechanics [2, 52] and it is commonly referred to as *ultraweak coupling* [49].

Under these assumptions every composite energy eigenstate $|s_k\rangle$ can be written as a product,

$$|s_k\rangle = |\mathfrak{s}_k\rangle \otimes |\mathfrak{b}_k\rangle, \tag{1.68}$$

where the states $|\mathfrak{s}_k\rangle$ and $|\mathfrak{b}_k\rangle$ are energy eigenstates in $\mathfrak{S}$ and $\mathfrak{B}$, respectively. At this point envariance is crucial in our treatment: all orthonormal bases are equivalent under envariance. Therefore, we can choose $|s_k\rangle$ as energy eigenstates of H.

For the canonical formalism we are now interested in the number of states accessible to the total system $\mathcal{S}$ under the condition that the total internal energy E (1.66) is given and constant. When the subsystem of interest, $\mathfrak{S}$, happens to be in a particular energy eigenstate $|\mathfrak{s}_k\rangle$ then the internal energy of the subsystem is given by the corresponding energy eigenvalue $\mathfrak{e}_k$. Therefore, for the total energy E to be constant, the energy of the heat bath, $E_{\mathfrak{B}}$, has to obey,

$$E_{\mathfrak{B}}(\mathfrak{e}_k) = E - \mathfrak{e}_k. \tag{1.69}$$

This condition can only be met if the energy spectrum of the heat reservoir is at least as dense as the one of the subsystem.

The number of states, $\mathfrak{N}(\mathfrak{e}_k)$, accessible to $\mathcal{S}$ is then given by the fraction

$$\mathfrak{N}(\mathfrak{e}_k) = \frac{\mathfrak{N}_{\mathfrak{B}}(E - \mathfrak{e}_k)}{\mathfrak{N}_{\mathcal{S}}(E)}, \tag{1.70}$$

where $\mathfrak{N}_{\mathcal{S}}(E)$ is the total number of states in $\mathcal{S}$ consistent with equation (1.66), and $\mathfrak{N}_{\mathfrak{B}}(E - \mathfrak{e}_k)$ is the number of states available to the heat bath, $\mathfrak{B}$, determined by condition (1.69). In other words, we are asking for nothing else but the degeneracy in $\mathfrak{B}$ corresponding to a particular energy state of the system of interest $|\mathfrak{s}_k\rangle$.

Example: composition of multiple qubits

The idea is most easily illustrated with a simple example, before we derive the general formula in the following paragraph. Imagine a system of interest, $\mathfrak{S}$, that interacts with N non-interacting qubits with energy eigenstates $|0\rangle$ and $|1\rangle$ and corresponding eigenenergies $e_0^{\mathfrak{B}}$ and $e_1^{\mathfrak{B}}$. Note once again that the composite states $|s_k\rangle$ can always be chosen to be energy eigenstates, since the even composite state $|\psi_{\mathcal{SE}}\rangle$ (1.64) is envariant under all unitary operations on $\mathcal{S}$.

We further assume the qubits to be non-interacting. Therefore, all energy eigenstates can be written in the form

$$|s_k\rangle = |\mathfrak{s}_k\rangle \otimes \underbrace{|\,\delta_k^1 \delta_k^2 \cdots \delta_k^N\,\rangle}_{N-qubits}. \tag{1.71}$$

Here $\delta_k^i \in \{0, 1\}$ for all $i \in 1, \ldots, N$ describing the states of the bath qubits. Let us denote the number of qubits of $\mathfrak{B}$ in $|0\rangle$ by n. Then the total internal energy E becomes a simple function of n and is given by,

$$E = \mathfrak{e}_k + n\, e_0^{\mathfrak{B}} + (N - n)\, e_1^{\mathfrak{B}}. \tag{1.72}$$

Now it is easy to see that the total number of states corresponding to a particular value of E, i.e. the degeneracy in $\mathfrak{B}$ corresponding to $\mathfrak{e}_k$, (1.70) is given by,

$$\mathfrak{N}(\mathfrak{e}_k) = \frac{N!}{n!\,(N - n)!}. \tag{1.73}$$

Equation (1.73) describes nothing else but the number of possibilities to distribute $ne_0^{\mathfrak{B}}$ and $(N - n)e_1^{\mathfrak{B}}$ over N qubits.

It is worth emphasizing that in the arguments leading to equation (1.73) we explicitly used that the $|s_k\rangle$ are energy eigenstates in $\mathcal{S}$ and the subsystem $\mathfrak{S}$ and heat reservoir $\mathfrak{B}$ are non-interacting. The first condition is not an assumption, since the composite $|\psi_{\mathcal{SE}}\rangle$ is envariant under all unitary maps on $\mathcal{S}$, and the second condition is in full agreement with conventional assumptions of thermodynamics [2, 52].

Boltzmann's formula for the canonical state

The example treated in the preceding section can be easily generalized. We again assume that the heat reservoir $\mathfrak{B}$ consists of N non-interacting subsystems with identical eigenvalue spectra $\{e_j^{\mathfrak{B}}\}_{j=1}^m$. In this case the internal energy (1.69) takes the form

$$E = \mathfrak{e}_k + n_1\, e_1^{\mathfrak{B}} + n_2\, e_2^{\mathfrak{B}} + \cdots + n_m e_m^{\mathfrak{B}}, \tag{1.74}$$

with $\sum_{j=1}^m n_j = N$. Therefore, the degeneracy (1.70) becomes

$$\mathfrak{N}(\mathfrak{e}_k) = \frac{N!}{n_1! n_2! \cdots n_m!}. \tag{1.75}$$

This expression is readily recognized as a quantum envariant formulation of Boltzmann's counting formula for the number of classical microstates [53], which quantifies the volume of phase space occupied by the thermodynamic state. However, instead of having to equip phase space with an (artificial) equispaced grid, we simply count degenerate states.

We are now ready to derive the Boltzmann–Gibbs formula. To this end consider that in the limit of very large, $N \gg 1$, $\mathfrak{N}(\mathfrak{e}_k)$ (1.75) can be approximated with Stirling's formula. We have

$$\ln\left(\mathfrak{N}(\mathfrak{e}_k)\right) \simeq N \ln\left(N\right) - \sum_{j=1}^m n_j \ln\left(n_j\right). \tag{1.76}$$

As pointed out earlier, thermodynamic equilibrium states are characterized by a maximum of symmetry or maximal number of 'involved energy states', which corresponds classically to a maximal volume in phase space. In the case of the microcanonical equilibrium this condition was met by the state that is maximally envariant, namely envariant under all unitary maps. Now, following Boltzmann's line of thought we identify the canonical equilibrium by the configuration of the heat reservoir $\mathfrak{B}$ for which the maximal number of energy eigenvalues are occupied. Under the constraints,

$$\sum_{j=1}^m n_j = N \quad \text{and} \quad E - \mathfrak{e}_k = \sum_{j=1}^m n_j\, e_j^{\mathfrak{B}} \tag{1.77}$$

this problem can be solved by variational calculus. One obtains

$$n_j = \mu \, \exp\!\left(\beta\, e_j^{\mathfrak{B}}\right), \tag{1.78}$$

which is the celebrated Boltzmann–Gibbs formula. Notice that equation (1.78) is the number of states in the heat reservoir $\mathfrak{B}$ with energy $e_j^{\mathfrak{B}}$ for $\mathfrak{S}$ and $\mathfrak{B}$ being in thermodynamic, canonical equilibrium. In this treatment temperature merely enters through the Lagrangian multiplier β.

What remains to be shown is that β, indeed, characterizes the unique temperature of the system of interest, $\mathfrak{S}$. To this end, imagine that the total system $\mathcal{S}$ can be

separated into two small systems $\mathfrak{S}_1$ and $\mathfrak{S}_2$ of comparable size, and the thermal reservoir, $\mathfrak{B}$. It is then easy to see that the total number of accessible states $\mathfrak{N}(\mathfrak{e}_k)$ does not significantly change in comparison to the previous case. In particular, in the limit of an infinitely large heat bath $\mathfrak{B}$ the total number of accessible states for $\mathfrak{B}$ is still given by equation (1.75). In addition, it can be shown that the resulting value of the Lagrange multiplier, β, is unique [57]. Hence, we can formulate a statement of the zeroth law of thermodynamics from envariance—namely, two systems $\mathfrak{S}_1$ and $\mathfrak{S}_2$, that are in equilibrium with a large heat bath $\mathfrak{B}$, are also in equilibrium with each other, and they have the same temperature corresponding to the unique value of β.

The present discussion is exact, up to the approximation with the Stirling's formula, and only relies on the fact that the total system $\mathcal{S}$ is in a microcanonical equilibrium as defined in terms of envariance, equation (1.68). The final derivation of the Boltzmann–Gibbs formula (1.78), however, requires additional thermodynamic conditions. In the case of the microcanonical equilibrium we replaced conventional arguments by maximal envariance, whereas for the canonical state we required the maximal number of energy levels of the heat reservoir to be 'occupied'.

1.4 Work, heat, and entropy production

Equipped with a classical understanding of thermodynamic phenomenology, the fluctuation theorems (1.23) and understanding of equilibrium states from a fully quantum theory, we can now move on to define work, heat, and entropy production for quantum systems. The following treatment was first published in reference [18].

1.4.1 Quantum work and quantum heat

Quasistatic processes
In complete analogy to the standard framework of thermodynamics as discussed in section 1.1, we begin the discussion by considering quasistatic processes during which the quantum system, $\mathcal{S}$, is always in equilibrium with a thermal environment. However, we now further assume that the Hamiltonian of the system, $H(\lambda)$, is parameterized by a control parameter λ. The parameter can be, e.g. the volume of a piston, the angular frequency of an oscillator, the strength of a magnetic field, etc.

Generally, the dynamics of $\mathcal{S}$ is then described by the Liouville type equation $\dot{\rho} = L_\lambda(\rho)$, where the superoperator L_λ reflects both the unitary dynamics generated by H and the non-unitary contribution induced by the interaction with the environment. We further have to assume that the equation for the steady state, $L_\lambda(\rho^{ss}) = 0$, has a unique solution [49] to avoid any ambiguities. As before, we will now be interested in thermodynamic state transformations, for which $\mathcal{S}$ remains in equilibrium corresponding to the value of λ.

Thermodynamics of Gibbs equilibrium states
As we have seen above, in the the limit of ultraweak coupling the equilibrium state is given by the Gibbs state,

$$\rho^{\mathrm{eq}} = \exp(-\beta H)/Z, \quad \text{where} \quad Z = \mathrm{tr}\{\exp(-\beta H)\}, \tag{1.79}$$

and where β is the inverse temperature of the environment. In this case, the thermodynamic entropy is given by the Gibbs entropy [2], $S = -\mathrm{tr}\{\rho^{\mathrm{eq}} \ln(\rho^{\mathrm{eq}})\} = \beta(E - F)$, whereas before $E = \mathrm{tr}\{\rho^{\mathrm{eq}} H\}$ is the internal energy of the system, and $F = -1/\beta \ln(Z)$ denotes the Helmholtz free energy.

For isothermal, quasistatic processes the change of thermodynamic entropy dS can be written as

$$dS = \beta \,(\mathrm{tr}\{d\rho^{\mathrm{eq}}\, H\} + (\mathrm{tr}\{\rho^{\mathrm{eq}}\, dH\} - dF)) = \beta \,\mathrm{tr}\{d\rho^{\mathrm{eq}}\, H\}, \tag{1.80}$$

where the second equality follows from simply evaluating terms. Therefore, two forms of energy can be identified [21]: heat is the change of internal energy associated with a change of entropy; work is the change of internal energy due to the change of an extensive parameter, i.e. change of the Hamiltonian of the system. We have,

$$dE = đQ + đW \equiv \mathrm{tr}\{d\rho^{\mathrm{eq}}\, H\} + \mathrm{tr}\{\rho^{\mathrm{eq}}\, dH\}. \tag{1.81}$$

The identification of heat $đQ$, and work $đW$ (1.81) is consistent with the second law of thermodynamics for quasistatic processes (1.5) *if*, and as we will shortly see, *only if* ρ^{eq} is a Gibbs state (1.79).

It is worth emphasizing that for isothermal, quasistatic processes we further have,

$$dS = \beta \,đQ \quad \text{and} \quad dF = đW, \tag{1.82}$$

for which the first law of thermodynamics takes the form

$$dE = T \,dS + dF. \tag{1.83}$$

In this particular formulation it becomes apparent that changes of the internal energy dE can be separated into 'useful' work dF and an additional contribution, $T \,dS$, reflecting the *entropic cost* of the process.

Thermodynamics of non-Gibbsian equilibrium states

As we have seen above in section 1.3, however, quantum systems in equilibrium are only described by Gibbs states (1.79) if they are ultraweakly coupled to the environment. Typically, quantum systems are correlated with their surroundings and interaction energies are *not* negligible [20, 22, 25]. For instance, it has been seen explicitly in the context of quantum Brownian motion [24] that system and environment are generically entangled.

In such situations the identification of heat only with changes of the state of the system (1.81) is no longer correct [22]. Rather, to formulate thermodynamics consistently the energetic back-action due to the correlation of system and environment has to be taken into account [22, 24]. This means that during quasistatic processes parts of the energy exchanged with the environment are not related to a change of the thermodynamic entropy of the system, but rather constitute the energetic price to maintain the non-Gibbsian state, i.e. coherence and correlations between system and environment.

Denoting the non-Gibbsian equilibrium state by ρ^{ss} we can write

$$\begin{aligned}
\mathcal{H} &= -\operatorname{tr}\{\rho^{\text{ss}}\ln(\rho^{\text{ss}})\} + (\operatorname{tr}\{\rho^{\text{ss}}\ln(\rho^{\text{eq}})\} - \operatorname{tr}\{\rho^{\text{ss}}\ln(\rho^{\text{eq}})\}) \\
&= \beta[E - (F + T\,S(\rho^{\text{ss}}\|\rho^{\text{eq}}))] = \beta\,(\mathcal{E} - \mathcal{F}),
\end{aligned} \tag{1.84}$$

where, as before, $E = \operatorname{tr}\{\rho^{\text{ss}}H\}$ is the internal energy of the system, and $\mathcal{F} \equiv F + T\,S(\rho^{\text{ss}}\|\rho^{\text{eq}})$ is the so-called the information free energy [42]. Further, $S(\rho^{\text{ss}}\|\rho^{\text{eq}}) \equiv \operatorname{tr}\{\rho^{\text{ss}}(\ln(\rho^{\text{ss}}) - \ln(\rho^{\text{eq}}))\}$ is the quantum relative entropy [55].

In complete analogy to the standard, Gibbsian case (1.81) we now consider isothermal, quasistatic processes, for which the infinitesimal change of the entropy reads

$$\begin{aligned}
d\mathcal{H} &= \beta\,[\operatorname{tr}\{d\rho^{\text{ss}}H\} + (\operatorname{tr}\{\rho^{\text{ss}}dH\} - d\mathcal{F})] \\
&\equiv \beta\,(\text{\dj}Q_{\text{tot}} - \text{\dj}Q_{\text{c}})
\end{aligned} \tag{1.85}$$

where we identified the total heat as $\text{\dj}Q_{\text{tot}} \equiv \operatorname{tr}\{d\rho^{\text{ss}}H\}$ and energetic price to maintain coherence and quantum correlations as $\text{\dj}Q_{\text{c}} \equiv d\mathcal{F} - \operatorname{tr}\{\rho^{\text{ss}}dH\}$.

The *excess heat* $\text{\dj}Q_{\text{ex}}$ is the only contribution that is associated with the entropic cost,

$$d\mathcal{H} = \beta\,\text{\dj}Q_{\text{ex}}, \quad \text{and} \quad \text{\dj}Q_{\text{ex}} = \text{\dj}Q_{\text{tot}} - \text{\dj}Q_{\text{c}}. \tag{1.86}$$

Accordingly, the first law of thermodynamics takes the form

$$dE = \text{\dj}W_{\text{ex}} + \text{\dj}Q_{\text{ex}} \tag{1.87}$$

where $\text{\dj}W_{\text{ex}} \equiv \text{\dj}W + \text{\dj}Q_{\text{c}}$ is the excess work. Finally, equation (1.81) generalizes for isothermal, quasistatic processes in generic quantum systems to

$$dE = T\,d\mathcal{H} + d\mathcal{F}. \tag{1.88}$$

It is worth emphasizing at this point once again that thermodynamics is a phenomenological theory, and as one expects, the fundamental relations hold for any physical system. Equation (1.88) has exactly the same form as equation (1.81), however, the 'symbols' have to be interpreted differently when translating between the thermodynamic relations and the underlying statistical mechanics.

As an immediate consequence of this analysis, we can now derive the efficiency of any quantum system undergoing a Carnot cycle.

Universal efficiency of quantum Carnot engines

To this end, imagine a generic quantum system that operates between two heat reservoirs with hot, T_{hot}, and cold, T_{cold}, temperatures, respectively. Then, the Carnot cycle consists of two isothermal processes during which the system absorbs/exhausts heat and two thermodynamically adiabatic, i.e. isentropic strokes while the extensive control parameter λ is varied.

During the first isothermal stroke, the system is put into contact with the hot reservoir. As a result, the excess heat $Q_{\text{ex},1}$ is absorbed at temperature T_{hot} and excess work $W_{\text{ex},1}$ is performed,

$$W_{ex,1} = \mathcal{F}(\lambda_2, T_{hot}) - \mathcal{F}(\lambda_1, T_{hot})$$
$$Q_{ex,1} = T_{hot}\left(\mathcal{H}(\lambda_2, T_{hot}) - \mathcal{H}(\lambda_1, T_{hot})\right). \tag{1.89}$$

Next, during the isentropic stroke, the system performs work $W_{ex,2}$ and no excess heat is exchanged with the reservoir, $\Delta\mathcal{H} = 0$. Therefore, the temperature of the engine drops from T_{hot} to T_{cold},

$$W_{ex,2} = \Delta E = E(\lambda_3, T_{cold}) - E(\lambda_2, T_{hot})$$
$$= \Delta\mathcal{F} - (T_{hot} - T_{cold})\,\mathcal{H}(\lambda_3, T_{cold}). \tag{1.90}$$

In the second line, we employed the thermodynamic identity $E = \mathcal{F} + T\,\mathcal{H}$, which follows from the definition of $\mathcal{F}$. During the second isothermal stroke, the excess work $W_{ex,3}$ is performed on the system by the cold reservoir. This allows for the system to exhaust the excess heat $Q_{ex,3}$ at temperature T_{cold}. Hence we have

$$W_{ex,3} = \mathcal{F}(\lambda_4, T_{cold}) - \mathcal{F}(\lambda_3, T_{cold})$$
$$Q_{ex,3} = T_{cold}(\mathcal{H}(\lambda_c, T_{cold}) - \mathcal{H}(\lambda_3, T_{cold})). \tag{1.91}$$

Finally, during the second isentropic stroke, the cold reservoir performs the excess work $W_{ex,4}$ on the system. No excess heat is exchanged and the temperature of the engine increases from T_{cold} to T_{hot},

$$W_{ex,4} = \Delta E = E(\lambda_1, T_{hot}) - E(\lambda_4, T_{cold})$$
$$= \Delta\mathcal{F} + (T_{hot} - T_{cold})\,\mathcal{H}(\lambda_1, T_{hot}). \tag{1.92}$$

The efficiency of a thermodynamic device is defined as the ratio of 'output' to 'input'. In the present case the 'output' is the total work performed during each cycle, i.e. the total excess work, $W_{ex} = W + Q_c$. There are two physically distinct contributions: work in the usual sense, W, that can be utilized, e.g. to power external devices, and Q_c, which cannot serve such purposes as it is the thermodynamic cost to maintain the non-Gibbsian equilibrium state. Therefore, the only thermodynamically consistent definition of the efficiency is

$$\eta = \frac{\sum_i W_{ex,i}}{Q_{ex,1}} = 1 - \frac{T_{cold}}{T_{hot}} \equiv \eta_C, \tag{1.93}$$

which is identical to the classical Carnot efficiency.

1.4.2 Quantum entropy production

Having established a conceptual framework for quantum work and heat, the next natural step is to determine the *quantum entropy production*. To this end, we now imagine that $\mathcal{S}$ is initially prepared in an equilibrium state which, however, is not necessarily a Gibbs state (1.79) with respect to the temperature of the environment. For a variation of the external control parameter λ we can write the change of internal energy ΔE and a change of the von Neumann entropy as

$$\Delta E = W + Q \quad \text{and} \quad \Delta \mathcal{H} = \beta Q + \Sigma, \tag{1.94}$$

where here Q is the total heat exchanged during the process with the environment at inverse temperature β. Thus, we can write for the mean nonequilibrium entropy production,

$$\Sigma = \Delta \mathcal{H} - \beta \Delta E + \beta W. \tag{1.95}$$

Now, expressing the internal energy with the help of the Gibbs state ρ^{eq} (1.79) we have

$$\beta E = \beta \, \mathrm{tr}\{\rho^{\mathrm{ss}} H\} = -\mathrm{tr}\{\rho^{\mathrm{ss}} \ln(\rho^{\mathrm{eq}})\} + \ln(Z), \tag{1.96}$$

Thus, we can write for a process that varies λ from λ_0 to λ_1 (compare with the classical expression (1.39) and the quantum case (1.81))

$$\begin{aligned}
\beta W &= \beta \int_{\lambda_0}^{\lambda_1} d\lambda \, \mathrm{tr}\{\rho^{\mathrm{ss}}(\lambda) \, \partial_\lambda H(\lambda)\} \\
&= -\int_{\lambda_0}^{\lambda_1} d\lambda \, \mathrm{tr}\{\rho^{\mathrm{ss}}(\lambda) \, \partial_\lambda \ln(\rho^{\mathrm{eq}}(\lambda))\} - \ln(Z_1) + \ln(Z_0).
\end{aligned} \tag{1.97}$$

Combining equations (1.95)–(1.97), we obtain the general expression for the entropy production along a nonequilibrium path (compare figure 1.2),

$$\begin{aligned}
\Sigma &= S(\rho^{\mathrm{ss}}(\lambda_0)||\rho^{\mathrm{eq}}(\lambda_0)) - S(\rho^{\mathrm{ss}}(\lambda_1)||\rho^{\mathrm{eq}}(\lambda_1)) \\
&\quad - \int_{\lambda_0}^{\lambda_1} d\lambda \, \mathrm{tr}\{\rho^{\mathrm{ss}}(\lambda) \, \partial_\lambda \ln(\rho^{\mathrm{eq}}(\lambda))\}.
\end{aligned} \tag{1.98}$$

Equation (1.98) is the exact microscopic expression for the mean nonequilibrium entropy production for a driven open quantum system weakly coupled to a single heat reservoir. It is valid for intermediate states that can be arbitrarily far from equilibrium.

1.4.3 Two-time energy measurement approach

Having identified expressions for the average, work, heat, and entropy production, we can now continue building *quantum stochastic thermodynamics*. In complete analogy to the classical case, quantum stochastic thermodynamics is built upon fluctuation theorems. Conceptually, the most involved problem is how to identify heat and work for single realizations—and even what a 'single realization' means for a quantum system.

The most successful approach has become known as two-time energy measurement approach [3]. In this paradigm, one considers an isolated quantum system that evolves under the time-dependent Schrödinger equation

$$i\hbar \, \partial_t |\psi_t\rangle = H_t \, |\psi_t\rangle. \tag{1.99}$$

As before, we are interested in describing thermodynamic processes that are induced by varying an external control parameter λ_t during time τ, so that $H_t = H(\lambda_t)$.

Within the two-time energy measurement approach quantum work is determined by the following protocol: at initial time $t = 0$ a projective energy measurement is performed on the system; then the system is let to evolve under the time-dependent Schrödinger equation, before a second projective energy measurement is performed at $t = \tau$.

Therefore, work W becomes a stochastic variable, and for a single realization of this protocol we have

$$W[|m\rangle; |n\rangle] = E_m(\lambda_0) - E_n(\lambda_\tau), \tag{1.100}$$

where $|m\rangle$ is the initial eigenstate with eigenenergy $E_m(\lambda_0)$ and $|n\rangle$ with $E_n(\lambda_\tau)$ denotes the final state.

The distribution of work values is then given by averaging over an ensemble of realizations of the same process,

$$\mathcal{P}(W) = \langle \delta(W - W[|m\rangle; |n\rangle]) \rangle, \tag{1.101}$$

which can be rewritten as

$$\mathcal{P}(W) = \sum_{m,n} \int \delta(W - W[|m\rangle; |n\rangle]) \, p(|m\rangle \to |n\rangle). \tag{1.102}$$

In the latter equation the symbol $\sum\!\!\!\!\int$ denotes that we have to sum over the discrete part of the eigenvalue spectrum and integrate over the continuous part. Therefore, for systems with spectra that have both contributions the work distribution will have a continuous part and delta-peaks, see for instance for the Morse oscillator in reference [37].

Further, $p(|m\rangle \to |n\rangle)$ denotes the probability to observe a specific transition $|m\rangle \to |n\rangle$. This probability is given by [37],

$$p(|m\rangle \to |n\rangle) = \text{tr}\{\Pi_n \, U_\tau \, \Pi_m \, \rho^{\text{eq}} \, \Pi_m \, U_\tau^\dagger\}, \tag{1.103}$$

where ρ^{eq} is the initial, Gibbsian density operator (1.79) of the system[2], and U_τ is the unitary time-evolution operator, $U_\tau = \mathcal{T}_> \exp(-i/\hbar \int_0^\tau dt \, H_t)$. Finally, Π_ν denotes the projector into the space spanned by the νth eigenstate. For Hamiltonians with non-degenerate spectra we simply have $\Pi_\nu = |\nu\rangle\langle\nu|$.

The quantum Jarzynski equality
It is then a relatively simple exercise to show that such a definition of quantum work fulfills a quantum version of the Jarzynski equality. To this end, we compute the average of the exponentiated work

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[2] Generally, the initial state can be chosen according to the physical situation. However, in quantum stochastic thermodynamics it is often convenient to assume an initially thermal state.

$$\langle \exp(-\beta W) \rangle = \int dW \ \mathcal{P}(W) \exp(-\beta W)$$
$$= \sum_{m,n} \exp(\beta \ W[|m\rangle; \ |n\rangle]) \ p(|m\rangle \rightarrow |n\rangle). \tag{1.104}$$

Using the explicit expression for the transition probabilities (1.103) and for the Gibbs state (1.79), we immediately have

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F). \tag{1.105}$$

The latter theorem looks analogous to the classical Jarzynski equality (1.45). However, quantum work is a markedly different quantity than work in classical mechanics. It has been pointed out that work as defined from the two-time measurement is not a quantum observable in the usual sense, namely that there is no Hermitian operator whose eigenvalues are the classical work values [50, 51]. The simple reason is that the final Hamiltonian does not necessarily commute with the initial Hamiltonian, $[H_\tau, H_0] \neq 0$. Rather, quantum work is given by a time-ordered correlation function, which reflects that thermodynamically work is a non-exact, i.e. path dependent quantity.

Neglected informational cost
Another issue arises from the fact that generally the final state ρ_τ is a complicated nonequilibrium state. This means, in particular, that also $\rho_\tau = \rho(\lambda_\tau)$ does not commute with the final Hamiltonian H_τ, and one has to consider the back-action on the system due to the projective measurement of the energy [38]. For a single measurement, Π_n, the post-measurement state is given by $\Pi_n \rho_\tau \Pi_n / p_n$, where $p_n = \text{tr}\{\Pi_n \rho_\tau\}$. Thus, the system can be found on average in

$$\rho_\tau^M = \sum_n \Pi_n \, \rho_\tau \, \Pi_n. \tag{1.106}$$

Accordingly, the final measurement of the energy is accompanied by a change of information, i.e. by a change of the von Neumann entropy of the system

$$\Delta \mathcal{H}^M = -\text{tr}\left\{\rho_\tau^M \ln\left(\rho_\tau^M\right)\right\} + \text{tr}\{\rho_\tau \ln(\rho_\tau)\} \geqslant 0. \tag{1.107}$$

Information, however, is physical [33] and its acquisition 'costs' work. This additional work has to be paid by the external observer—the measurement device. In a fully consistent thermodynamic framework this cost should be taken into consideration.

Quantum work without measurements
To remedy this conceptual inconsistency arising from neglecting the informational contribution of the projective measurements, an alternative paradigm has been proposed [11]. For isolated systems quantum work is clearly given by the change of internal energy. As a statement of the first law of thermodynamics this holds true no matter whether the system is measured or not.

Actually, for thermal, Gibbs states (1.79) measuring the energy is superfluous as state and energy commute. Hence, an alternative notion of quantum work can be formulated that is fully based on the time evolution of energy eigenstates. Quantum work for a single realization is then determined by considering how much the expectation value for a single energy eigenstate changes under the unitary evolution. Hence, we define

$$\tilde{W}_m \equiv \langle m | U_\tau^\dagger \, H_\tau \, U_\tau | m \rangle - E_m(\lambda_0). \tag{1.108}$$

We can easily verify that the so-defined quantum work (1.108), indeed, fulfills the first law. To this end, we compute the average work $\langle W \rangle_{\tilde{\mathcal{P}}}$,

$$\begin{aligned}
\langle W \rangle_{\tilde{\mathcal{P}}} &= \oint_m \langle m | U_\tau^\dagger \, H_\tau \, U_\tau | m \rangle \, p_m - \text{tr}\{\rho_0^{\text{eq}} \, H_0\} \\
&= \text{tr}\{\rho_\tau^{\text{ss}} \, H_\tau\} - \text{tr}\{\rho_0^{\text{eq}} \, H_0\} = \langle W \rangle,
\end{aligned} \tag{1.109}$$

where $p_m = \exp(-\beta \, E_m(\lambda_0))/Z_0$ is the probability to find the system in the mth eigenstate at time $t = 0$. It is important to note that the average quantum work determined from two-time energy measurements is identical to the (expected) value given only knowledge from a single measurement at $t = 0$. Most importantly, however, in this paradigm the external observer does not have to pay a thermo-dynamic cost associated with the change of information due to measurements.

Modified quantum Jarzynski equality
We have now seen that the first law of thermodynamics is immune to whether the energy of the system is measured or not, since projective measurements of the energy do not affect the internal energy. However, the informational content of the system of interest, i.e. the entropy, crucially depends on whether the system is measured. Therefore, we expect that the statements of the second law have to be modified to reflect the informational contribution [10]. In this paradigm the modified quantum work distribution becomes

$$\tilde{\mathcal{P}}(W) = \oint_m \delta(W - \tilde{W}_m) \, p_m, \tag{1.110}$$

where, as before, $p_m = \exp(-\beta \, E_m(\lambda_0))/Z_0$. Now, we can compute the average exponentiated work,

$$\langle \exp(-\beta W) \rangle_{\tilde{\mathcal{P}}} = \frac{1}{Z_0} \oint_m \exp\!\left(-\beta \, \langle m | U_\tau^\dagger \, H_\tau \, U_\tau | m \rangle\right). \tag{1.111}$$

The right side of equation (1.111) can be interpreted as the ratio of two partition functions, where Z_0 describes the initial thermal state. The second partition function,

$$\tilde{Z}_\tau \equiv \oint_m \exp\!\left(-\beta \, \langle m | U_\tau^\dagger \, H_\tau, \, U_\tau | m \rangle\right) \tag{1.112}$$

corresponds to the best possible guess for a thermal state of the final system given only the time-evolved energy eigenbasis. This state can be written as

$$\tilde{\rho}_\tau \equiv \frac{1}{\tilde{Z}_\tau} \oint_m \exp\left(-\beta \langle m|U_\tau^\dagger H_\tau U_\tau|m\rangle\right) U_\tau|m\rangle\langle m|U_\tau^\dagger, \tag{1.113}$$

which differs from the true thermal state, $\rho_\tau^{eq} = \exp(-\beta H_\tau)/Z_\tau$.

As noted above, in information theory the 'quality' of such a best possible guess is quantified by the relative entropy [55], which measures the distinguishability of two (quantum) states. Hence, let us consider

$$S(\tilde{\rho}_\tau||\rho_\tau^{eq}) = \text{tr}\left\{\tilde{\rho}_\tau \ln(\tilde{\rho}_\tau)\right\} - \text{tr}\left\{\tilde{\rho}_\tau \ln\left(\rho_\tau^{eq}\right)\right\}, \tag{1.114}$$

for which we compute both terms separately. For the first term, the negentropy of $\tilde{\rho}_\tau$ we obtain,

$$\text{tr}\left\{\tilde{\rho}_\tau \ln(\tilde{\rho}_\tau)\right\} = -\ln(\tilde{Z}) - \beta \text{ tr}\left\{\tilde{\rho}_\tau \oint_m \langle m|U_\tau^\dagger H_\tau U_\tau|m\rangle U_\tau|m\rangle\langle m|U_\tau^\dagger\right\}$$
$$= -\ln(\tilde{Z}) - \beta\tilde{E}, \tag{1.115}$$

where we introduced the expected value of the energy, $\tilde{E}$, under the time-evolved eigenstates,

$$\tilde{E} = \frac{1}{\tilde{Z}} \oint_m \exp\left(-\beta \langle m|U_\tau^\dagger H_\tau U_\tau|m\rangle\right)\langle m|U_\tau^\dagger H_\tau U_\tau|m\rangle. \tag{1.116}$$

The second term, the cross entropy of $\tilde{\rho}_\tau$ and ρ_τ^{eq}, simplifies to

$$\text{tr}\left\{\tilde{\rho}_\tau \ln\left(\rho_\tau^{eq}\right)\right\} = -\ln(Z_\tau) - \beta \text{ tr}\left\{\oint_m \frac{1}{\tilde{Z}} \exp\left(-\beta \langle m|U_\tau^\dagger H_\tau U_\tau|m\rangle U_\tau|m\rangle\langle m|U_\tau^\dagger H_\tau\right)\right\} \tag{1.117}$$
$$= -\ln(Z_\tau) - \beta\tilde{E}.$$

Hence, the modified quantum Jarzynski equality (1.111) becomes

$$\langle \exp(-\beta W)\rangle_{\tilde{\mathcal{P}}} = \exp(-\beta\Delta F)\exp\left(-S\left(\tilde{\rho}_\tau\big|\big|\rho_\tau^{eq}\right)\right), \tag{1.118}$$

where, as before, $\Delta F = -1/\beta \ln(Z_\tau/Z_0)$. Jensen's inequality further implies,

$$\beta \langle W\rangle \geqslant \beta \Delta F + S\left(\tilde{\rho}_\tau\big|\big|\rho_\tau^{eq}\right) \tag{1.119}$$

where we used $\langle W\rangle_{\tilde{\mathcal{P}}} = \langle W\rangle$.

By defining quantum work as an average over time-evolved eigenstates we obtain a modified quantum Jarzynski equality (1.111) and a generalized maximum work theorem (1.119), in which the thermodynamic cost of projective measurements becomes apparent. These results become even more transparent by noting that

similar versions of the maximum work theorem have been derived in the thermo-dynamics of information [42]. As mentioned above, it has proven useful to introduce the notion of an information free energy,

$$\tilde{F}_\tau = F_\tau + S\!\left(\tilde{\rho}_\tau \middle\| \rho_\tau^{\text{eq}}\right)\!\Big/\beta. \tag{1.120}$$

Here, $\tilde{F}_\tau$ accounts for the additional capacity of a thermodynamic system to perform work due to information [10]. Note that in equation (1.120) $\tilde{F}_\tau$ is computed for the fictitious equilibrium state $\tilde{\rho}_\tau$.

We can rewrite equation (1.119) as

$$\beta\,\langle W \rangle \geqslant \beta\,\Delta\tilde{F}. \tag{1.121}$$

The latter inequality constitutes a sharper bound than the usual maximum work theorem, and it accounts for the extra free energy available to the system. Free energy, however, describes the usable, extractable work. In real-life applications one is more interested in the maximal free energy the system has available, than in the work that could be extracted by intermediate, disruptive measurements of the energy. Therefore, this treatment could be considered thermodynamically more relevant than the two-time measurement approach.

1.4.4 Quantum fluctuation theorem for arbitrary observables

Another issue with the two-time energy measurement approach is that in many experimental situations projective measurements of the energy are neither feasible nor practical. Rather, only other observables such as the spatial density or the magnetization are accessible. Then, the natural question is whether there is a fluctuation theorem for the observable that can actually be measured.

To answer this question, let us consider a more general paradigm, which was first published in reference [30]: information about a quantum system and its dynamics is obtained by performing measurements on $\mathcal{S}$ at the beginning and end of a specific process. Initially a quantum measurement is made of observable Ω^i, with eigenvalues ω_m^i. As before, Π_m^i denote the orthogonal projectors into the eigenspaces of Ω^i, and we have $\Omega^i = \sum_m \omega_m^i \Pi_m^i$. Note that the eigenvalues $\{\omega_m^i\}$ can be degenerate, so the projectors Π_m^i may have rank greater than one. Unlike the classical case, as long as ρ_0 and Ω^i do not have a common set of eigenvectors—i.e. they do not commute—performing a measurement on $\mathcal{S}$ alters its statistics. Measuring ω_m^i maps ρ_0 to the state $\Pi_m^i \rho_0 \Pi_m^i / p_m$, where $p_m = \text{tr}_{\{}\Pi_m^i \rho_0 \Pi_m^i\}$ is the probability of the measurement outcome ω_m^i. Generally accounting for all possible measurement outcomes, the statistics of $\mathcal{S}$ after the measurement are given by the weighted average of all projections,

$$M^i(\rho_0) = \sum_m \Pi_m^i \, \rho_0 \, \Pi_m^i. \tag{1.122}$$

If ρ_0 commutes with Ω^i, it commutes with each Π_m^i, so $M^i(\rho_0) = \sum_m \Pi_m^i \Pi_m^i \rho_0 = \rho_0$ and the statistics of the system are unaltered by the measurement. After measuring

ω_m^i, $\mathcal{S}$ undergoes a generic time evolution, after which it is given by $\mathbb{E}(\Pi_m^i \rho_0 \Pi_m^i)/p_m$. Here $\mathbb{E}$ represents any linear (unitary or non-unitary) quantum transformation, which is trace-preserving and maps non-negative operators to non-negative operators. Moreover, we require that this holds whenever $\mathbb{E}$ is extended to an operation $\mathbb{E} \otimes \mathbb{I}_{\mathcal{E}}$ on any enlarged Hilbert space $\mathcal{H}_S \otimes \mathcal{H}_{\mathcal{E}}$ ($\mathbb{I}_{\mathcal{E}}$ being the identity map on $\mathcal{H}_{\mathcal{E}}$). Such a transformation is called a completely positive, trace-preserving (CPTP) map [38].

After this evolution, a measurement of a second (not necessarily the same) observable, $\Omega^f = \sum_n \omega_n^f \Pi_n^f$, is performed on $\mathcal{S}$. The probability of measuring ω_n^f, conditioned on having first measured ω_m^i, is $p_{n|m} = \mathrm{tr}\{\Pi_n^f \mathbb{E}(\Pi_m^i \rho_0 \Pi_m^i)\}/p_m$. Accordingly, the joint probability distribution $p_{m \to n}$ reads

$$p(|m\rangle \to |n\rangle) = p_m \cdot p_{n|m} = \mathrm{tr}\left\{\Pi_n^f \, \mathbb{E}\big(\Pi_m^i \rho_0 \Pi_m^i\big)\right\}. \tag{1.123}$$

We are interested in the probability distribution of possible measurement outcomes, $\mathcal{P}(\Delta\omega)$, where $\Delta\omega_{n,m} = \omega_n^f - \omega_m^i$ is a random variable determined in a single measurement run. Its probability distribution is given by averaging over all possible realizations,

$$\mathcal{P}(\Delta\omega) = \langle \delta\big(\Delta\omega - \Delta\omega_{n,m}\big)\rangle = \sum_{m,n} \delta\big(\Delta\omega - \Delta\omega_{n,m}\big) \, p(|m\rangle \to |n\rangle). \tag{1.124}$$

To derive the integral fluctuation theorem we follow another standard approach and compute its characteristic function, $\mathcal{G}(s)$, which is the Fourier transform of $\mathcal{P}(\Delta\omega)$ [3]

$$\begin{aligned}\mathcal{G}(s) &= \int d(\Delta\omega) \, \mathcal{P}(\Delta\omega) \, \exp(is \, \Delta\omega) \\ &= \mathrm{tr}\left\{\exp(is\Omega^f) \, \mathbb{E}\big(M^i(\rho_0)\exp(-is\Omega^i)\big)\right\}.\end{aligned} \tag{1.125}$$

Choosing $s = i$, we obtain the identity

$$\langle \exp(-\Delta\omega)\rangle = \varepsilon. \tag{1.126}$$

Since it is explicitly dependent on the map $\mathbb{E}$, the quantity ε accounts for the information *lost* by not measuring the environment,

$$\varepsilon = \mathrm{tr}\left\{\exp(-\Omega^f) \, \mathbb{E}\big(M^i(\rho_0)\exp(\Omega^i)\big)\right\}. \tag{1.127}$$

which has been called the *quantum efficacy*.

We emphasize that equation (1.126) is *not* an integral fluctuation theorem in the strict sense. Generally, the quantum efficacy (1.127) explicitly depends on the choice of the observables, Ω^i and Ω^f, the initial state ρ_0, and the CPTP map $\mathbb{E}$. In a fluctuation theorem the right-hand side, i.e. ε should be a c-number independent of the details of the measurement protocol.

However, it is also easy to see when equation (1.126) becomes a fluctuation theorem. This is the case, if the initial state ρ_0 is proportional to $\exp(-\Omega^i)$, and if the CPTP map is unital, which means $\mathbb{E}(\mathbb{I}) = \mathbb{I}$. These conditions are naturally fulfilled

for initial Gibbs states (1.79), energy measurements, and unitary Schrödinger dynamics. However, we also immediately observe that the quantum Jarzynski equality (1.105) remains valid in purely decohering or purely dephasing models [1, 19, 43, 44, 47].

1.4.5 Quantum entropy production in phase space

We conclude this section with an alternative approach to stochastic thermodynamics of quantum systems, which was first published in reference [8]. We have seen above that for classical systems the irreversible entropy production is defined along a path in phase space (1.43). If we want to define an analogous entropy production for a quantum process, we have to choose a representation of quantum phase space.

A particularly convenient representation of quantum states is given by the Wigner function [58],

$$\mathcal{W}_t(x, p) = \frac{1}{2\pi\hbar} \int dy \, \exp\left(-\frac{i}{\hbar} py\right) \left\langle x + \frac{y}{2} \middle| \rho_t \middle| x - \frac{y}{2} \right\rangle. \tag{1.128}$$

The Wigner function contains the full classical information, and its marginals are the probability distributions for the position x and the momentum p, respectively. In addition, $\mathcal{W}_t(x, p)$ contains the full quantum information about a state, as, e.g. areas in phase space where $\mathcal{W}_t(x, p)$ takes negative values are indicative for quantum interference.

In complete analogy to the classical case, the quantum Liouville equation can be written as

$$\partial_t \, \mathcal{W}(\Gamma, t) = \mathcal{L}_\lambda \, \mathcal{W}(\Gamma, t), \tag{1.129}$$

where $\Gamma = (x, p)$ denotes again a point in phase space. It is worth emphasizing that a Liouvillian, $\mathcal{L}_\lambda$, does not generally exist for all quantum systems. In particular, for a thermally open harmonic oscillator it was shown in [31] that the existence and explicit form of $\mathcal{L}_\lambda$ are determined by the initial preparation of the environment.

The stationary solution of equation (1.129) is determined by

$$\mathcal{L}_\lambda \, \mathcal{W}_{\text{stat}}(\Gamma, \lambda) = 0. \tag{1.130}$$

Generally the stationary Wigner function $\mathcal{W}_{\text{stat}}(\Gamma, \lambda)$ for an open quantum system in equilibrium is not given by the Wigner representation of the Gibbs state (1.79). For instance, the exact master equation for a harmonic oscillator coupled to an environment consisting of an ensemble of harmonic oscillators is known [25] and can be solved analytically [16]. In a high-temperature approximation the quantum Liouville equation (1.129) becomes, in leading order of $\hbar$, [13]

$$\mathcal{L}_t = -\frac{p}{m} \, \partial_x + V'(x, t) \, \partial_p \, + \partial_p\big(\gamma p + D_{pp} \, \partial_p\big) + D_{xp} \, \partial^2_{xp} \tag{1.131}$$

where γ is again the coupling coefficient to the environment, $D_{pp} = m\gamma/\beta + m\beta\gamma\hbar^2(\omega^2 - \gamma^2)/12$, and $D_{xp} = \beta\gamma\hbar^2/12$. Note that in the high-temperature limit,

$\beta\hbar\omega \ll 1$, equation (1.131) reduces to the classical Klein–Kramers equation (1.34). The stationary solution can be written as

$$\mathcal{W}_{\text{stat}}(x, p) = \frac{m\gamma\omega}{2\pi} \frac{1}{\sqrt{D_{pp}(D_{pp} + m\gamma\, D_{xp})}} \exp\left(-\frac{\gamma}{2}\left(\frac{p^2}{D_{pp}} + \frac{m^2\omega^2\, x^2}{D_{pp} + m\gamma\, D_{xp}}\right)\right). \quad (1.132)$$

We will now prove that the quantum entropy production Σ for *any* quantum dynamics described by equation (1.129) and defined as

$$\Sigma[\Gamma_\tau; \lambda_\tau] \equiv -\int_0^\tau dt\, \dot{\lambda}_t\, \frac{\partial_\lambda \mathcal{W}_{\text{stat}}(\Gamma_t, \lambda_t)}{\mathcal{W}_{\text{stat}}(\Gamma_t, \lambda_t)}, \quad (1.133)$$

fulfills an integral fluctuation theorem. Note that writing Σ as a functional of a trajectory in (quantum) phase space is a mathematical construct, which is convenient for the following proof. More formally, we understand the entropy produced along a quantum trajectory in analogy to Feynman path integrals. Here a quantum trajectory is a mathematical tool defined as a generalization of the classical trajectory. Physical quantities are given by averages over an ensemble of such trajectories.

Consider the accumulated entropy σ produced up to time t, $\sigma(t) = -\int_0^t ds\, \dot{\lambda}_s\, \partial_\lambda \mathcal{W}_{\text{stat}}/\mathcal{W}_{\text{stat}}$, and thus $\sigma(\tau) = \Sigma$. Then the joint (quasi) probability distribution for the point in phase space and the accumulated entropy production, $P(\Gamma, \sigma, t)$, evolves according to,

$$\partial_t P(\Gamma, \sigma, t) = [\mathcal{L}_\lambda - j_{\text{stat}}(\Gamma, \lambda_t)\, \partial_\sigma]\, P(\Gamma, \sigma, t), \quad (1.134)$$

where $j_{\text{stat}}(\Gamma, \lambda_t)$ is the (quasi) probability flux associated with the accumulated entropy production σ,

$$j_{\text{stat}}(\Gamma, \lambda_t) = \dot{\lambda}_t\, \frac{\partial_\lambda \mathcal{W}_{\text{stat}}(\Gamma, \lambda_t)}{\mathcal{W}_{\text{stat}}(\Gamma, \lambda_t)}. \quad (1.135)$$

Now we define the auxiliary density $\Psi(\Gamma, t)$ which is the exponentially weighted marginal of $P(\Gamma, \sigma, t)$. We have

$$\Psi(\Gamma, t) = \int d\sigma\, P(\Gamma, \sigma, t)\, \exp(-\sigma), \quad (1.136)$$

for which the evolution equation (1.134) becomes

$$\partial_t \Psi(\Gamma, t) = [\mathcal{L}_\lambda - j_{\text{stat}}(\Gamma, \lambda_t)]\, \Psi(\Gamma, t). \quad (1.137)$$

It is easy to see that a solution of equation (1.137) is given by the stationary solution of the original master equation (1.129) and we obtain

$$\Psi(\Gamma, t) = \mathcal{W}_{\text{stat}}(\Gamma, \lambda_t). \quad (1.138)$$

Using the normalization of the stationary Wigner function we calculate with the latter solution for $\Psi(\Gamma, t)$,

$$1 = \int d\Gamma \, \mathcal{W}_{\text{stat}}(\Gamma, \lambda_\tau) = \int d\Gamma \, \Psi(\Gamma, \tau) = \langle \exp(-\Sigma) \rangle, \qquad (1.139)$$

which concludes the proof. For any quantum system, open or closed, the entropy production fulfilling an integral fluctuation theorem is given by equation (1.133).

1.5 Checklist for 'The principles of modern thermodynamics'

1. Thermodynamics is a phenomenological theory to describe the average behavior of heat and work.
2. Reversible processes can be understood as paths on the thermodynamic manifold described by the equation of state.
3. Systems can be locally in equilibrium and at the same time not in equilibrium with the rest of the Universe.
4. Heat, work, and entropy can be defined along single trajectories of classical systems.
5. Fluctuation theorems are symmetry relations for the distribution of work values expressing that 'violations' of the second law are exponentially unlikely.
6. Statistical mechanics can be built from a purely quantum framework using symmetries of entanglement.
7. Quantum work is not an observable in the usual sense.
8. There are many different and equally justifiable notions of quantum work and entropy production.

1.6 Problems

A phenomenological theory of heat and work (section 1.1)

[1] Consider a single quantum particle in an infinite square well, and whose density operator is a Gibbs state. Compute the equation of state for the length of the box L, the temperature T, and the mass m, and plot the thermodynamic manifold. How does the manifold change if an additional (identical) particle is added? Does it matter whether the particles are fermions of bosons?

[2] Quantum heat engines are thermodynamic devices with small quantum systems as working medium. A stereotypical example is a single quantum particle trapped in a harmonic potential. The natural external control parameter is the angular frequency. Determine the equation of state assuming that the quantum particle is ultraweakly coupled to a thermal environment, which means the density operator is a Gibbs state. Compute the efficiency of such a device as it undergoes an Otto cycle.

The advent of stochastic thermodynamics (section 1.2)

[1] Consider a one-dimensional, classical harmonic oscillator, whose dynamics is described by the classical Liouville equation (1.40). Compute the probability density function of the work done during a variation of the angular frequency, if the oscillator was initially prepared in a Maxwell–Boltzmann distribution. Verify the Jarzynski equality (1.45).

[2] Consider a one-dimensional classical harmonic oscillator in contact with a thermal bath, whose dynamics is described by the classical Klein–Kramers equation (1.34). Compute the probability density function of the work while dragging the oscillator along the x-axis, if the oscillator was initially prepared in a Maxwell–Boltzmann distribution. Verify the Crooks fluctuation theorem (1.58).

Foundations of statistical physics from quantum entanglement (section 1.3)

[1] Illustrate the concept of envariance for a Universe consisting of two harmonic oscillators and parity preserving unitary maps.

[2] Repeat the arguments leading to equation (1.78), but by including the next two terms of the Stirling approximation

$$\ln(n!) \simeq n \ln(n) - n + \frac{1}{2} \ln(2\pi n) + \frac{1}{12\,n}.$$

How would one identify the temperature in this case?

Work, quantum heat, and quantum entropy production (section 1.4)

[1] Consider a thermally isolated, quantum harmonic oscillator in one dimension. Compute the probability density function for the work done during an infinitely slow variation of the angular frequency, if the oscillator was initially prepared in a Gibbs state.

[2] Consider a one-dimensional quantum harmonic oscillator in contact with a thermal bath, whose dynamics is described by the quantum Klein–Kramers equation (1.131). Compute the probability density function of the entropy production while dragging the oscillator along the x-axis. Verify the quantum fluctuation theorem (1.139).

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Chapter 1

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