

Quantum Thermodynamics

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April 5, 2023

The theory of quantum thermodynamics investigates how the concepts of heat, work, and temperature can be carried over to the quantum realm, where fluctuations and randomness are fundamentally unavoidable. This lecture provides an introduction to the thermodynamics of small quantum systems. After illustrating how the laws of thermodynamics emerge from quantum theory we will discuss how open quantum systems can be modeled by Markovian master equations. We then consider models of quantum systems that are designed to perform a certain task, such as cooling or generating entanglement. Finally, we investigate how fluctuations can be taken into account in a thermodynamic description by extending the laws of thermodynamics.

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I. Introduction

By investigating concepts such as heat, work, and temperature, the theory of thermodynamics was a driving force in the industrial revolution, enabling the improvement and development of technologies that reshaped society such as steam engines and refrigerators [1]. Quantum thermodynamics investigates heat, work, temperature, as well as related concepts in quantum systems. In analogy to macroscopic thermodynamics, this endeavor promises to enable the development and improvement of novel quantum- and nano-technologies. Furthermore, a good understanding of the thermodynamics of quantum systems is key for keeping the energetic footprint of any scalable quantum technology in check [2].

As the concepts investigated by quantum thermodynamics are very general, the theory is of relevance for essentially all scenarios involving open quantum systems. This makes the field

extremely broad, including well established topics such as thermoelectricity [3, 4], investigating how an electrical current arises from a temperature gradient, as well as very recent investigations into the energetics of single qubit gates [5]. The broad nature of the field implies that the quantum thermodynamics community brings together people with very different backgrounds.

This course is meant to provide an introduction to this diverse and fast-growing field, introducing fundamental concepts and illustrating them with simple examples. After a short introduction to basic concepts, macroscopic thermodynamics, and information theory in Sec. I, Sec. II will address the topic of thermodynamic equilibrium. This will allow for understanding why a system may often be described by very few parameters, such as temperature and chemical potential, and it will give you a physical understanding of these fundamental parameters. Section III will then discuss how the laws of thermodynamics emerge from quantum mechanics, connecting these very general laws to the microscopic behavior of a quantum system. Applying the laws of thermodynamics to quantum systems will allow you to make general predictions on what happens when small systems are placed into contact with thermal reservoirs. This may improve your physical intuition for how systems in and out of equilibrium behave, which is an extremely valuable skill as a physicist. In Sec. IV, we will study quantum master equations as a tool to describe open quantum systems. This is an extremely useful and versatile tool that can be employed to model many of the physical scenarios investigated at the University of Basel including, e.g., quantum dots, NV centers, and optical cavities. Section V will then investigate quantum thermal machines, exploring some of the tasks that can be achieved with open quantum systems. Such tasks include the production of work, refrigeration, and the creation of entanglement. Finally, in Sec. VI, we will consider fluctuations which become important in nano-scale systems. You will learn how thermodynamic considerations may result in equalities and inequalities that can be understood as extensions of the laws of thermodynamics, determining the behavior of fluctuations around average values.

Further reading: As recently as 2022, a textbook on quantum stochastic thermodynamics by Strasberg was published [6]. While similar in spirit to the material discussed in this course, the book has a stronger focus on fluctuations which are only covered in Sec. VI in this course. Another good resource is the book published in 2019 by Deffner and Campbell [7]. Compared to this lecture, it has a stronger focus on information-theoretic concepts and thermodynamic cycles. A slightly older textbook on the topic was published in 2009 by Gemmer, Michel, and Mahler [8]. While being a valuable resource for many of the concepts, it predates a number of important works that are central to how the topic is presented here. In addition, in 2019 a book giving a snapshot of the field was published, providing numerous short reviews on different topics by over 100 contributing authors [9]. Furthermore, a number of excellent reviews focusing on different aspects of quantum thermodynamics are provided by Refs. [3, 4, 10–14]. These resources are complemented by the focus issue in Ref. [15].

I.1. Basic concepts

In this section, we introduce some basic concepts that are used throughout the course. We set $\hbar = 1$ throughout the course. Note that this section should mainly act as a reminder (with the possible exception of Sec. I.3) and to set the notation. If a concept is completely new to you, I suggest to read up on it in the respective references, which provide a far more detailed introduction.

I.1.1. Linear algebra

Because linear algebra provides the mathematical description of quantum mechanics, we review some basic concepts here. In a format accessible for physicists, a more detailed introduction can be found in most textbooks on quantum mechanics, see, e.g., Sec. 1 in the book by Shankar [16] or Sec. 2.1 in the book by Nielsen and Chuang [17].

Vectors in Hilbert spaces: A (pure) quantum state can be described by a vector in a complex Hilbert space \mathcal{H} , which is a vector space equipped with an inner product. Such vectors may be denoted by

$$|\psi\rangle, \quad |\varphi\rangle, \quad a|\psi\rangle + b|\varphi\rangle, \quad (1)$$

where a and b are complex numbers. For reasons that will become clear later, we also call a vector a *ket*. Any vector can be written using a set of linearly independent basis vectors $|j\rangle$ as

$$|\psi\rangle = \sum_j \psi_j |j\rangle. \quad (2)$$

Linear operators: Vectors can be manipulated by operators. A linear operator $\hat{A} : \mathcal{H} \rightarrow \mathcal{H}'$ maps a vector from a Hilbert space, \mathcal{H} , onto another vector, potentially in another Hilbert space \mathcal{H}' , i.e., $\hat{A}|\psi\rangle$ is a vector in \mathcal{H}' for any $|\psi\rangle \in \mathcal{H}$. Furthermore, a linear operator obeys

$$\hat{A}(a|\psi\rangle + b|\varphi\rangle) = a\hat{A}|\psi\rangle + b\hat{A}|\varphi\rangle. \quad (3)$$

Dual vectors: For each vector, a dual vector (an element of the dual space \mathcal{H}^*) exists given by the Hermitian conjugate of the original vector

$$\langle\psi| = |\psi\rangle^\dagger. \quad (4)$$

A dual vector is also called a *bra*. The notation introduced in Eqs. (1) and (4) is called Dirac or bra-ket notation.

Inner product: The inner product between two vectors $|\psi\rangle$ and $|\varphi\rangle$ is given by

$$\langle\psi|\varphi\rangle \in \mathbb{C}, \quad (5)$$

and is a complex number. Note that this makes any dual vector a linear operator mapping vectors onto the Hilbert space of complex numbers, i.e., $\langle\psi| : \mathcal{H} \rightarrow \mathbb{C}$. With the inner product, we may define an orthonormal basis $|j\rangle$ as one fulfilling

$$\langle i|j\rangle = \delta_{i,j}, \quad (6)$$

where $\delta_{i,j}$ denotes the Kronecker delta. Using Eq. (2), we may express any vector through an orthonormal basis. The inner product between two vectors may then be evaluated as

$$\langle\psi|\varphi\rangle = \left(\sum_j \psi_j^* \langle j| \right) \left(\sum_k \varphi_k |k\rangle \right) = \sum_j \psi_j^* \varphi_j. \quad (7)$$

Row and column vectors: Every complex vector space of finite dimension n is isomorphic to \mathbb{C}^n . What this means is that as long as we consider finite-dimensional Hilbert spaces, we may use conventional row and column vectors. For instance, a set of orthonormal basis vectors may be identified by column vectors with the j -th entry equal to one and all others equal to zero. General vectors can then be expressed through Eq. (2), i.e.,

$$|j\rangle \equiv \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \quad \langle j| \equiv (\cdots \quad 0 \quad 1 \quad 0 \quad \cdots), \quad \Rightarrow \quad |\psi\rangle \equiv \begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix}, \quad \langle\psi| \equiv (\psi_0^* \quad \psi_1^* \quad \psi_2^* \quad \cdots). \quad (8)$$

Matrices and the resolution of the identity: An important operator is the identity operator $\mathbb{1}$ defined by

$$\mathbb{1} |\psi\rangle = |\psi\rangle \quad \forall \quad |\psi\rangle. \quad (9)$$

Using any orthonormal basis, the identity may be written

$$\mathbb{1} = \sum_j |j\rangle\langle j|. \quad (10)$$

This equation is called the *resolution of the identity* and it is heavily used in deriving various results in quantum mechanics. With its help, we may express an operator in the basis of $|j\rangle$ as

$$\hat{A} = \sum_{j,k} |j\rangle\langle j| \hat{A} |k\rangle\langle k| = \sum_{j,k} A_{jk} |j\rangle\langle k|, \quad (11)$$

where $A_{jk} = \langle j| \hat{A} |k\rangle$ are the matrix elements of \hat{A} . Indeed, with the help of the row and column vectors in Eq. (8), we may identify

$$\hat{A} \equiv \begin{pmatrix} A_{00} & A_{01} & \cdots \\ A_{10} & A_{11} & \\ \vdots & & \ddots \end{pmatrix}, \quad \hat{A}^\dagger \equiv \begin{pmatrix} A_{00}^* & A_{10}^* & \cdots \\ A_{01}^* & A_{11}^* & \\ \vdots & & \ddots \end{pmatrix}, \quad (12)$$

and we recover the usual prescription for the Hermitian conjugate of matrices.

1.1.2. The density matrix

The density matrix describes the state of a quantum system and is thus a central object throughout this lecture and in quantum theory in general. A more detailed introduction can be found in the book by Nielsen and Chuang [17], see Sec. 2.4.

The state of a quantum system is described by a positive semi-definite operator with unit trace acting on the Hilbert space \mathcal{H} . Positive semi-definite means that all eigenvalues of the density matrix are larger or equal to zero and unit trace means that the eigenvalues add up to one. The density matrix may be written as

$$\hat{\rho} = \sum_j p_j |\psi_j\rangle\langle\psi_j|, \quad \text{with} \quad \langle\psi_j|\psi_j\rangle = 1, \quad p_j \geq 0, \quad \sum_j p_j = 1. \quad (13)$$

We may interpret the density matrix as the system being in the pure state $|\psi_j\rangle$ with probability p_j . If multiple p_j are non-zero, this describes a scenario of incomplete knowledge. This is illustrated in the following examples.

Classical mixture vs quantum superposition: Let us first consider the toss of a coin, where we identify with $|0\rangle$ the outcome tails and with $|1\rangle$ the outcome heads. The outcome of such a coin toss (before observation) is described by the density matrix

$$\hat{\rho} = \frac{1}{2} (|0\rangle\langle 0| + |1\rangle\langle 1|) = \mathbb{1}, \quad (14)$$

which is equal to the identity matrix, also called the maximally mixed state because each outcome is equally likely. Such a mixture of states is completely classical and merely reflects a scenario of incomplete knowledge, in this case the outcome of the coin toss.

We now compare the state in Eq. (14) to a quantum superposition provided by the pure state $|+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$

$$\hat{\rho} = |+\rangle\langle +| = \frac{1}{2} (|0\rangle\langle 0| + |1\rangle\langle 1| + |0\rangle\langle 1| + |1\rangle\langle 0|). \quad (15)$$

In contrast to the maximally mixed state, this quantum state is pure and we thus have perfect knowledge of the system. Performing a projective measurement on this state in the basis $|\pm\rangle$ will with certainty result in $+$. However, the state describes a coherent superposition of the states $|0\rangle$ and $|1\rangle$. This coherent superposition is distinguished from a mixture by the off-diagonal elements $|0\rangle\langle 1|$ and $|1\rangle\langle 0|$ (also called coherences).

Time evolution of an isolated system: The time-evolution of a system that is isolated from its environment is given by

$$\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(0)\hat{U}^\dagger(t), \quad \hat{U}(t) = \mathcal{T}e^{-i\int_0^t dt' \hat{H}(t')}, \quad (16)$$

where $\hat{H}(t)$ is the Hamiltonian of the system and \mathcal{T} denotes the time-ordering operator. The time-ordered exponential appearing in Eq. (16) can be written as

$$\mathcal{T}e^{-i\int_0^t dt' \hat{H}(t')} = \lim_{\delta t \rightarrow 0} e^{-i\delta t \hat{H}(t)} e^{-i\delta t \hat{H}(t-\delta t)} e^{-i\delta t \hat{H}(t-2\delta t)} \dots e^{-i\delta t \hat{H}(2\delta t)} e^{-i\delta t \hat{H}(\delta t)} e^{-i\delta t \hat{H}(0)}, \quad (17)$$

such that the time argument in the Hamiltonian on the right-hand side increases from the right to the left of the expression. Each exponential in the product can be understood as the time-evolution by the infinitesimal time-step δt [18].

Note that in quantum mechanics, a system that is isolated from its environment is denoted as a closed system. This can be confusing in the field of quantum thermodynamics because in thermodynamics, a closed system traditionally refers to a system that can exchange energy but cannot exchange matter with its environment. To avoid confusion, I try to use the term *isolated system* throughout this lecture.

I.1.3. Second quantization

Many scenarios considered in this course feature the transport of electrons or photons through a quantum system. Such scenarios are most conveniently described using the formalism of second quantization, see Sec. 1 in the Book by Bruus and Flensberg [19] for a more detailed introduction.

We first introduce the commutator and anti-commutator which play important roles for bosons and fermions respectively

$$\begin{aligned} \text{Commutator:} & \quad [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}, \\ \text{Anti-commutator:} & \quad \{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}. \end{aligned} \quad (18)$$

Bosons: For a single bosonic mode, a central object is the creation operator \hat{a}^\dagger , which creates a boson in this mode. Its Hermitian conjugate \hat{a} denotes the annihilation operator, removing a boson from the mode. These operators obey the canonical commutation relations

$$[\hat{a}, \hat{a}^\dagger] = 1, \quad [\hat{a}, \hat{a}] = [\hat{a}^\dagger, \hat{a}^\dagger] = 0. \quad (19)$$

The state without any bosons is denoted the vacuum state $|0\rangle$ and by definition it is annihilated by the annihilation operator, $\hat{a}|0\rangle = 0$. The state with n bosons (also called a Fock state) can be written with help of the creation operator as

$$|n\rangle \equiv \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |0\rangle, \quad \langle n|m\rangle = \delta_{n,m}. \quad (20)$$

With these definitions, we find the action of the creation and annihilation operators on the Fock states

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad \hat{a}^\dagger\hat{a}|n\rangle = n|n\rangle. \quad (21)$$

The operator $\hat{n} \equiv \hat{a}^\dagger\hat{a}$ is called the number operator.

When dealing with multiple bosonic modes, we introduce subscripts on the annihilation operators \hat{a}_j . The canonical commutation relations then read

$$[\hat{a}_j, \hat{a}_k^\dagger] = \delta_{j,k}, \quad [\hat{a}_j, \hat{a}_k] = [\hat{a}_j^\dagger, \hat{a}_k^\dagger] = 0. \quad (22)$$

The number states can be written as

$$|n_0, n_1, \dots\rangle = |\mathbf{n}\rangle \equiv \prod_j \frac{(\hat{a}_j^\dagger)^{n_j}}{\sqrt{n_j!}} |0\rangle, \quad \hat{a}_j^\dagger\hat{a}_j|\mathbf{n}\rangle = n_j|\mathbf{n}\rangle. \quad (23)$$

Fermions: For a single fermionic mode, the creation and annihilation operators are denoted as \hat{c}^\dagger and \hat{c} respectively. In contrast to bosonic operators, they obey canonical anti-commutation relations

$$\{\hat{c}, \hat{c}^\dagger\} = 1, \quad \{\hat{c}, \hat{c}\} = \{\hat{c}^\dagger, \hat{c}^\dagger\} = 0. \quad (24)$$

The latter relation directly implies that $\hat{c}^2 = (\hat{c}^\dagger)^2 = 0$. A fermionic mode may thus at most be occupied by a single fermion. This is known as the Pauli exclusion principle. Just like for bosons, the vacuum state $|0\rangle$ is annihilated by the annihilation operator, $\hat{c}|0\rangle = 0$. The Fock states can then be written as

$$|1\rangle = \hat{c}^\dagger|0\rangle, \quad \hat{c}|1\rangle = |0\rangle, \quad \hat{c}^\dagger\hat{c}|n\rangle = n|n\rangle, \quad (25)$$

where $n = 0, 1$ and $\hat{c}^\dagger\hat{c}$ is called the number operator just like for bosons. Note that due to the Pauli exclusion principle, the occupied state $|1\rangle$ is annihilated by the creation operator $\hat{c}^\dagger|1\rangle = 0$, implying a symmetry between creation and annihilation operators. Indeed, we may call \hat{c}^\dagger the annihilation operator for a *hole* which has the vacuum state $|1\rangle$.

Multiple modes are denoted by an index and obey the canonical anti-commutation relations

$$\{\hat{c}_j, \hat{c}_k^\dagger\} = \delta_{j,k}, \quad \{\hat{c}_j, \hat{c}_k\} = \{\hat{c}_j^\dagger, \hat{c}_k^\dagger\} = 0. \quad (26)$$

Note that operators for different modes *anti*-commute, implying a sign change when exchanging two fermions. Just as for bosons, the number states can be written as

$$|n_0, n_1, \dots\rangle = |\mathbf{n}\rangle \equiv \prod_j \left(\hat{c}_j^\dagger\right)^{n_j} |0\rangle, \quad \hat{c}_j^\dagger \hat{c}_j |\mathbf{n}\rangle = n_j |\mathbf{n}\rangle. \quad (27)$$

Note however that do to the anti-commutation relations, the order with which \hat{c}_j^\dagger act on the vacuum in the last expression matters.

I.1.4. Exact and inexact differentials

Exact and inexact differentials play an important role in thermodynamics. They are introduced in most textbooks on thermodynamics, see for instance App. A of the book by Hentschke [20].

We recall that the differential of a differentiable function $f(x, y)$ of two variables is denoted by

$$df(x, y) = \partial_x f(x, y) dx + \partial_y f(x, y) dy, \quad (28)$$

where ∂_x denotes the partial derivative with respect to x , keeping y fixed. The integral of such a differential along any curve γ is determined solely by its endpoints

$$\int_\gamma df(x, y) = f(x_f, y_f) - f(x_i, y_i), \quad (29)$$

where the subscript i (f) denotes the initial (final) values of the curve γ .

We now consider a differential form

$$dg(x, y) = a(x, y) dx + b(x, y) dy. \quad (30)$$

We call this an exact differential if and only if

$$\partial_y a(x, y) = \partial_x b(x, y). \quad (31)$$

In that case, we may write $a(x, y) = \partial_x g(x, y)$ and $b(x, y) = \partial_y g(x, y)$ and $g(x, y)$ is a differentiable function. An exact differential is therefore a differential form that can be written as the differential of a function. We call the differential form in Eq. (30) an inexact differential if it cannot be written as the differential of a function. In this case, $\partial_y a(x, y) \neq \partial_x b(x, y)$. Importantly, the integral of an inexact differential generally does depend on the full curve and not just its endpoints.

As an example, we consider the exact differential

$$dz = y dx + x dy, \quad (32)$$

which is the differential of the function $z(x, y) = xy$. The differential in Eq. (32) can be written as the sum of two inexact differentials

$$\vec{d}q = y dx, \quad \vec{d}w = x dy, \quad (33)$$

where \vec{d} denotes an inexact differential. We may now integrate these differentials along two different curves with the same endpoints

$$\gamma_1 : (0, 0) \rightarrow (1, 0) \rightarrow (1, 1), \quad \gamma_2 : (0, 0) \rightarrow (0, 1) \rightarrow (1, 1). \quad (34)$$

Integrals along these paths may be evaluated using

$$\begin{aligned}\int_{\gamma_1} dg(x, y) &= \int_0^1 dx a(x, 0) + \int_0^1 dy b(1, y), \\ \int_{\gamma_2} dg(x, y) &= \int_0^1 dy a(0, y) + \int_0^1 dx b(x, 1),\end{aligned}\tag{35}$$

where we made use of Eq. (30). A simple calculation results in

$$\int_{\gamma_1} \vec{d}q = \int_{\gamma_2} \vec{d}w = 1, \quad \int_{\gamma_2} \vec{d}q = \int_{\gamma_1} \vec{d}w = 0.\tag{36}$$

As expected, we recover

$$\int_{\gamma_1} dz = \int_{\gamma_2} dz = z(1, 1) - z(0, 0) = 1.\tag{37}$$

I.2. Macroscopic thermodynamics

Here we briefly summarize some important aspects of the traditional theory of thermodynamics which applies at macroscopic scales, where fluctuations may safely be neglected. There are many textbooks on this topic, see for instance the books by Callen [21] or Hentschke [20].

Among physical theories, Thermodynamics takes a rather peculiar role because it is generally valid for all systems (at the macroscopic scale) and it does not provide numerical results but rather general equalities and inequalities which constrain physically allowed processes. Indeed, the theory of thermodynamics has been called the *village witch* among physical theories [12]. The main assumption in thermodynamics is that we can describe a macroscopic body by very few variables such as temperature T , pressure p , volume V , internal energy U , and entropy S , see Fig. 1. The macroscopic body may therefore be thought of as being in local equilibrium. Note however that the temperature of the body may be different from the temperature of the surroundings. Given these macroscopic variables, thermodynamics provides relations and constraints between them.

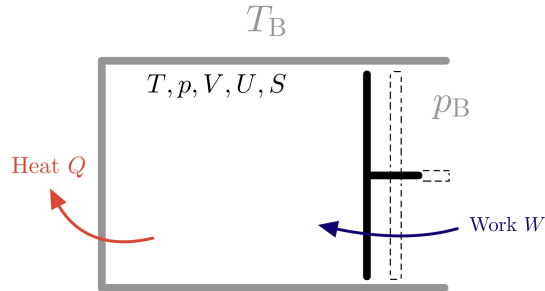


Figure 1: A gas in a container of volume V , at temperature T , with pressure p . The internal energy of the gas is given by U and its entropy by S . Using a piston, the volume of the gas can be changed and work W can be performed on the system. Energy may also be exchanged with the environment in the form of heat Q . Note that the temperature T_B and pressure p_B of the environment may differ from the temperature and pressure of the system.

The first law of thermodynamics: The first law of thermodynamics may be written in the form

$$dU = dW - dQ, \quad (38)$$

The first law states that energy is conserved and that energy changes come in two forms: heat dQ and work dW . Quite generally, work is a useful form of energy that is mediated by macroscopic degrees of freedom. This is in contrast to heat, which is a more inaccessible form of energy mediated by microscopic degrees of freedom. Note that these quantities are inexact differentials, i.e., they may depend on the curve taken when changing thermodynamic variables. Here we use a sign convention where work is positive when increasing the energy of the body while heat is positive when it flows out of the body and into the environment.

The first law of thermodynamics prevents a perpetuum mobile of the first kind, i.e., a machine that produces the work it needs to run itself indefinitely. In the presence of any type of losses, such a machine needs to produce work out of nothing, violating Eq. (38). An example would be a lamp that is powered by a solar cell, illuminated only by the lamp itself, see Fig. 2.

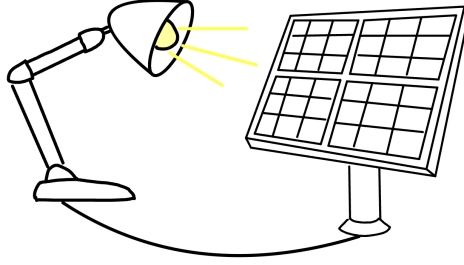


Figure 2: Perpetuum mobile of the first kind. A lamp illuminates a solar panel which in turn powers the lamp. Without any hidden energy source, such a device cannot work because of unavoidable losses. At long times, we may set $dU = 0$. Furthermore, we split the work $dW = dW_L - dW_S$, where W_L denotes the work exerted on the lamp by the solar panel and W_S denotes the work exerted on the solar panel by the lamp. In the presence of losses within the solar panel (any other loss mechanism results in similar conclusions), it provides strictly less work to the lamp than it received, i.e., $dW_L < dW_S$. By Eq. (38), this would necessitate another source of energy, either in the form of work or in the form of heat with $dQ < 0$.

Work may come in different forms. For instance, electrical work (also called chemical work) is produced when charges are moved from a region with lower voltage to a region with higher voltage, which is what happens when charging a battery. While this type of work will be the focus of later parts of this course, here we focus on the traditional example of mechanical work which is produced by changing the volume of a gas using, e.g., a piston as illustrated in Fig. 1. In this case, we know from classical mechanics that work is given by $dW = -p_B dV$, where p_B denotes the external pressure exerted by the piston. Furthermore, the heat flowing into the body can be related to the entropy change of the surrounding heat bath $dQ = T_B dS_B$. This relation follows from describing the heat bath as being in thermal equilibrium at temperature T_B and we will revisit this later in the course. We stress that in these expressions for heat and work, the quantities of the surrounding environment appear (dV only appears because $dV = -dV_B$).

The second law of thermodynamics: The second law of thermodynamics is provided by the Clausius inequality [22]

$$d\Sigma = dS + dS_B = dS + \sum_{\alpha} \frac{dQ_{\alpha}}{T_{\alpha}} \geq 0, \quad (39)$$

where we included multiple heat baths at respective temperature T_{α} that may exchange heat dQ_{α} with the body. The second law states that the total entropy, which is the sum of the entropy of the body S and the entropy of the surroundings $S_B = \sum_{\alpha} S_{\alpha}$, can only increase. This change in total entropy is called entropy production Σ .

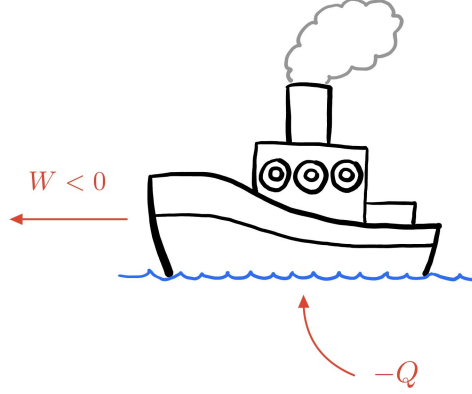


Figure 3: Perpetuum mobile of the second kind. A boat moves across the sea, being powered by the heat absorbed from the surrounding water. To move in the water, the boat needs to perform work against the friction force, i.e., $dW < 0$. At long times, we may neglect any changes in the internal energy or the entropy of the system, i.e., $dS = dU = 0$. The work required to move against the friction force must then be provided by heat coming from the environment, requiring $dQ < 0$. Since the environment only has a single temperature, this violates the second law of thermodynamics given in Eq. (39) which requires $dQ/T \geq 0$.

The second law of thermodynamics prevents a perpetuum mobile of the second kind, i.e., a machine that runs indefinitely by extracting heat out of an equilibrium environment. In this case, there is only one temperature T describing the environment. Furthermore, for long times we may neglect U as well as S since they remain finite while the produced work $-W$ increases indefinitely. The first law then requires $W = Q$ which when inserted in Eq. (39) provides $W/T \geq 0$, preventing any production of work. An example would be given by a boat that moves by extracting heat from the surrounding water, see Fig. 3. Note that dissipating work (i.e., turning work into heat, $W = Q \geq 0$) is perfectly allowed by the laws of thermodynamics and indeed is what happens when an incandescent light bulb is glowing.

In addition to this example, the second law of thermodynamics provides important limitations on physically allowed processes. Consider a heat engine, where the temperature gradient between two thermal baths at temperatures $T_h > T_c$ is exploited to produce work, see Fig. 4. Let us further consider a long-time scenario, where any changes in the system may be neglected compared to the heat and work which continuously increase. The first and second laws of thermodynamics then read

$$W = Q_h + Q_c, \quad \frac{Q_h}{T_h} + \frac{Q_c}{T_c} \geq 0. \quad (40)$$

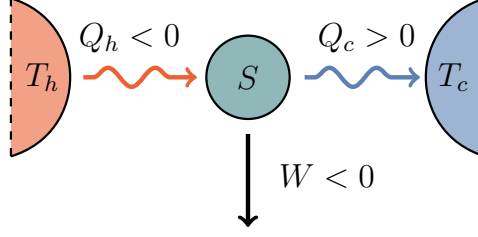


Figure 4: Working principle of a heat engine. Heat from a hot bath Q_h is partly converted into work W and partly dissipated into the cold bath Q_c . The dissipation ensures that the entropy production is positive, as required by the second law of thermodynamics, and limits the efficiency to be below the Carnot efficiency, see Eq. (41).

These equations have a few remarkable consequences. First, for $W = 0$ it is straightforward to show that $-Q_h = Q_c \geq 0$, i.e., heat flows out of the hot and into the cold bath. Second, either Q_h , Q_c , or both have to be positive, i.e., it is not possible to extract heat simultaneously from both baths. This is equivalent to the argument preventing a perpetual mobile of the second kind. A heat engine, defined by $-W > 0$ will thus require an influx of heat from the hot bath $Q_h < 0$, providing the necessary energy, as well as a heat outflux into the cold bath $Q_c > 0$ ensuring the increase in entropy. The second law of thermodynamics then implies the well-known result that the efficiency of such a heat engine is upper bounded by the Carnot efficiency

$$\eta \equiv \frac{-W}{-Q_h} \leq 1 - \frac{T_c}{T_h}. \quad (41)$$

Thermodynamic processes and cycles: In a thermodynamic process, the state of a body is changed by, e.g., changing its volume V or pressure p . Such changes can be applied under different conditions. For instance, in an *adiabatic* process, the state is changed without exchanging heat with the environment. Similarly, processes at constant temperature T or entropy S are called *isothermal* and *isentropic* processes respectively. Note that the word *adiabatic* is used differently in thermodynamics and in quantum mechanics. In quantum mechanics, it refers to processes that are sufficiently slow such that a system in its ground state remains in its groundstate throughout the process. For this reason, I will try to avoid the word *adiabatic*. An important class of thermodynamic processes are *reversible processes*, which obey $\Sigma = 0$. This generally requires that the body is in thermal equilibrium with its surroundings at all times. This implies that reversible processes have to be very slow and always are an idealization of any real process. As we will see below, reversible processes are very useful to derive thermodynamic relations.

By combining different thermodynamic processes, we can design thermodynamic cycles. After a completed cycle, the body is in the same state but since dQ and dW are inexact differentials, we generally have

$$\oint dU = 0, \quad \oint dQ = \oint dW \neq 0. \quad (42)$$

Thus, it is possible to turn heat into work in a thermodynamic cycle. Prominent examples of thermodynamic cycles are the Otto cycle, providing the underlying principle behind car

engines, and the Carnot engine, which is an idealized, reversible engine that reaches the Carnot efficiency given in Eq. (41).

Maxwell relations: Let us consider the first law of thermodynamics for a reversible process. As the body is in equilibrium with the environment throughout the process, we may identify $T = T_B$, $p = p_B$ and because $d\Sigma = 0$, we have $dS = -dS_B$. The first law thus reads

$$dU = TdS - pdV = \partial_S U dS + \partial_V U dV. \quad (43)$$

Since this is an exact differential, the last expression holds no matter if the process is reversible or not. However, the identification of heat and work with the first and second term on the right-hand side is only justified for reversible processes. Since U is a smooth function, partial derivatives with respect to different variables commute and we find the Maxwell relation

$$\partial_S \partial_V U = \partial_V \partial_S U = -\partial_S p. \quad (44)$$

Other Maxwell relations may be obtained similarly from other thermodynamic potentials such as the free energy $F = U - TS$. The free energy plays a particularly important role as it captures the capacity of a body to do work (in contrast to U capturing the capacity to provide heat and work). The differential of the free energy reads

$$dF = -SdT - pdV = \partial_T F dT + \partial_V F dV, \quad (45)$$

from which we may derive the Maxwell relation

$$-\partial_T \partial_V F = \partial_V \partial_T F = \partial_T p. \quad (46)$$

Equations of state: In order to obtain quantitative predictions, the theory of thermodynamics has to be supplemented by *equations of state*. For instance, a monatomic ideal gas with N atoms obeys the relations

$$U = \frac{3}{2} N k_B T, \quad pV = N k_B T, \quad (47)$$

where k_B denotes the Boltzmann constant. With the help of these equations, we may then derive non-trivial quantitative results such as the change in entropy when changing temperature and volume

$$S(T, V) - S(T_0, V_0) = k_B \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \right]. \quad (48)$$

I.3. Information theory

As we will see below, entropy is closely related to concepts from information theory. Here we provide a brief introduction to these concepts, for a more detailed discussion see for instance the original paper by Shannon [23] or the book by Cover and Thomas [24].

Self-information: Let us consider a random variable X with outcomes x_1, \dots, x_n occurring with probabilities p_1, \dots, p_n . Note that in this section, we use a different symbol for the random variable X and its outcomes x_j as is customary in mathematics. The *self-information* or *surprisal* of an outcome x_j is defined as

$$I_j = -\ln p_j. \quad (49)$$

It quantifies the information that is gained when observing outcome x_j . The self-information has the following properties:

- i) The less probable an event is, the more surprising it is and the more information we gain

$$\lim_{p_j \rightarrow 1} I_j = -\ln 1 = 0, \quad \lim_{p_j \rightarrow 0} I_j = \infty. \quad (50)$$

- ii) The information of uncorrelated events is additive. Let p_j^X and p_k^Y denote the probabilities that the independent random variables X and Y take on the values x_j and y_k respectively. It then holds that

$$p_{j,k} = p_j^X p_k^Y, \quad I_{j,k} = -\ln p_{j,k} = -\ln p_j^X - \ln p_k^Y = I_j^X + I_k^Y, \quad (51)$$

where $p_{j,k}$ denotes the joint probability of observing outcomes x_j and y_k .

We note that with Eq. (49), information is quantified in *nats* since we are using the natural logarithm. To quantify information in *bits*, one should use the logarithm of base 2 instead.

Shannon entropy: The Shannon entropy is defined as the average self-information

$$H = \sum_j p_j I_j = - \sum_j p_j \ln p_j. \quad (52)$$

It quantifies the average information gain when observing the random variable X , or, equivalently, the lack of information before observation. The practical importance of the Shannon entropy is highlighted by the *noiseless coding theorem* which states that storing a random variable taken from a distribution with Shannon entropy H requires at least H nats on average (if H is defined using \log_2 , then it requires at least H bits). Any further compression results in loss of information. This theorem can be illustrated using an example taken from Nielsen and Chuang [17]:

Consider a source that produces the symbols A , B , C , and D with respective probabilities $1/2$, $1/4$, $1/8$, and $1/8$. If we do not use any compression, we need two bits of storage per symbol, e.g.,

$$A \rightarrow 00, \quad B \rightarrow 01, \quad C \rightarrow 10, \quad D \rightarrow 11. \quad (53)$$

However, the symbols provided by the source may be encoded using less bits per symbol on average by taking into account the probability distribution of the source. The basic idea is to use less bits for the more frequent symbols. For instance, we may use the following encoding

$$A \rightarrow 0, \quad B \rightarrow 10, \quad C \rightarrow 110, \quad D \rightarrow 111. \quad (54)$$

Note that we cannot use $B \rightarrow 1$ because then we can no longer determine if 110 means C or if it means BBA . With this compression, we find the average number of bits per symbol to be $1/2 \cdot 1 + 1/4 \cdot 2 + 1/8 \cdot 3 + 1/8 \cdot 3 = 7/4$. This equals the Shannon entropy (in bits)

$$H = -\frac{1}{2} \log_2 \frac{1}{2} - \frac{1}{4} \log_2 \frac{1}{4} - \frac{1}{8} \log_2 \frac{1}{8} - \frac{1}{8} \log_2 \frac{1}{8} = \frac{7}{4}. \quad (55)$$

It turns out that any compression algorithm that uses less bits results in the loss of information.

Von Neumann entropy: The quantum version of the Shannon entropy is given by the von Neumann entropy

$$S_{\text{vN}}(\hat{\rho}) = -\text{Tr}\{\hat{\rho} \ln \hat{\rho}\} = -\sum_j p_j \ln p_j, \quad (56)$$

where $\hat{\rho} = \sum_j p_j |j\rangle\langle j|$. As a generalization of the Shannon entropy to quantum systems, it describes the lack of knowledge we have over a quantum system given a state $\hat{\rho}$. The von Neumann entropy is minimized for pure states and maximized for the maximally mixed state given by the identity matrix

$$S_{\text{vN}}(|\psi\rangle\langle\psi|) = 0, \quad S_{\text{vN}}(\mathbb{1}/d) = \ln d, \quad (57)$$

where d denotes the dimension of the Hilbert space.

Relative entropy: The relative entropy, also known as the *Kullback-Leibler divergence* [25] is useful to quantify information when a random variable is described by an erroneous distribution. For two distributions $\{p_j\}$ and $\{q_j\}$, the relative entropy is defined as

$$D_{\text{KL}} = \sum_j p_j \ln \frac{p_j}{q_j}. \quad (58)$$

By definition, $D_{\text{KL}} \geq 0$ where equality is only achieved if the two distributions are the same. To shed some light onto the interpretation of this quantity, let us assume that a random variable X is distributed according to $\{p_j\}$ but we describe it by the erroneous distribution $\{q_j\}$. The information gain that we attribute to the outcome x_j then reads $-\ln q_j$. On average, this gives

$$-\sum_j p_j \ln q_j = -\sum_j p_j \ln p_j + \sum_j p_j \ln \frac{p_j}{q_j} = H + D_{\text{KL}}. \quad (59)$$

The left-hand side of this equation provides information we assign to the random variable on average, the assumed information. The right-hand side provides the actual average information, given by the Shannon entropy, plus the relative entropy. The actual information is thus strictly smaller than the assumed information and the discrepancy between the assumed information and the actual information is quantified by the relative entropy. Since the assumed information is always larger than the actual information, we can think of the relative entropy as an *information loss* due to the erroneous description.

Quantum relative entropy: The generalization of the relative entropy to the quantum scenario is defined as [26]

$$S[\hat{\rho}||\hat{\sigma}] = \text{Tr}\{\hat{\rho} \ln \hat{\rho} - \hat{\rho} \ln \hat{\sigma}\}. \quad (60)$$

Just as its classical counterpart, it quantifies the discrepancy between the assumed and the actual lack of information when a system in state $\hat{\rho}$ is erroneously described by the state $\hat{\sigma}$. Just like the classical relative entropy, the quantum relative entropy is always non-negative $S[\hat{\rho}||\hat{\sigma}] \geq 0$.

II. Thermodynamic equilibrium

Equilibrium states may be characterized by a few intensive variables such as temperature T , chemical potential μ , and pressure p . In equilibrium, no net currents flow and the system is stationary, i.e., observables become time-independent. Note the similarity to the main assumption in macroscopic thermodynamics, see Sec. I.2. This is no coincidence. Indeed, in macroscopic thermodynamics, systems are assumed to be in local equilibrium (i.e., can be described by a thermal state with variables that may differ from the environment).

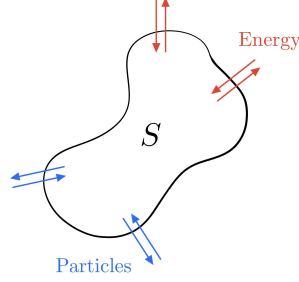


Figure 5: System exchanging energy and particles with the environment.

II.1. The grand-canonical ensemble

Throughout this lecture, we consider a system that may exchange both energy and particles with its surroundings as sketched in Fig. 5. In equilibrium, such a system is described by the grand-canonical Gibbs state

$$\hat{\rho}_G = \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{Z}, \quad Z = \text{Tr} \left\{ e^{-\beta(\hat{H} - \mu\hat{N})} \right\}, \quad (61)$$

where $\beta = 1/k_B T$ denotes the inverse temperature, \hat{H} is the Hamiltonian, \hat{N} the particle-number operator, and Z is called the partition function. For equilibrium states, we may generally identify the relevant quantities in macroscopic thermodynamics as average values

$$U \equiv \langle \hat{H} \rangle, \quad S \equiv k_B S_{\text{vN}}(\hat{\rho}). \quad (62)$$

Because the Gibbs state is of central importance for much that follows, we now discuss three different ways of motivating why it provides an adequate description for thermodynamic equilibrium.

II.1.1. Subsystem of an isolated system

The first motivation considers the system of interest to be a small part of a very large “supersystem” that is described as an isolated system, see Fig. 6. This motivation for the Gibbs state can be found in many textbooks, see e.g., Landau & Lifshitz [27] or Schwabl [28]. We start by assuming that the supersystem has a fixed energy and particle number given by E_{tot} and N_{tot} respectively. In this case, it is described by the so-called micro-canonical ensemble

$$\hat{\rho}_{\text{tot}} = \sum_{E,N} p_{\text{tot}}(E, N) |E, N\rangle\langle E, N|, \quad (63)$$

where $p_{\text{tot}}(E, N)$ is nonzero only if the energy and particle number are close to E_{tot} and N_{tot} , i.e., for $E_{\text{tot}} \leq E < E_{\text{tot}} + \delta E$ and $N_{\text{tot}} \leq N < N_{\text{tot}} + \delta N$. For energies and particle numbers within these shells, each state is equally likely in the microcanonical ensemble, i.e.,

$$p_{\text{tot}}(E, N) = \frac{\Theta(E - E_{\text{tot}})\Theta(N - N_{\text{tot}})\Theta(E_{\text{tot}} + \delta E - E)\Theta(N_{\text{tot}} + \delta N - N)}{\Omega(E_{\text{tot}}, N_{\text{tot}})\delta E\delta N}, \quad (64)$$

where $\Omega(E_{\text{tot}}, N_{\text{tot}})$ denotes the density of states and $\Theta(x)$ the Heaviside theta function which is equal to one for $x > 0$ and zero otherwise. Being a macroscopic supersystem, the number of states contributing to the microcanonical ensemble is assumed to be large

$$\Omega(E_{\text{tot}}, N_{\text{tot}})\delta E\delta N \gg 1. \quad (65)$$

At the same time, for energy and particle numbers to be well defined, we require $\delta E \ll E_{\text{tot}}$ and $\delta N \ll N_{\text{tot}}$. This also justifies to assume that the density of states is constant in the energy and particle number shells that contribute to the micro-canonical ensemble. For future reference, we note that the von Neumann entropy of the microcanonical ensemble is given by the logarithm of the number of contributing states [see also Eq. (57)]

$$S_{\text{vN}}(\hat{\rho}_{\text{tot}}) = \ln[\Omega(E_{\text{tot}}, N_{\text{tot}})\delta E\delta N]. \quad (66)$$

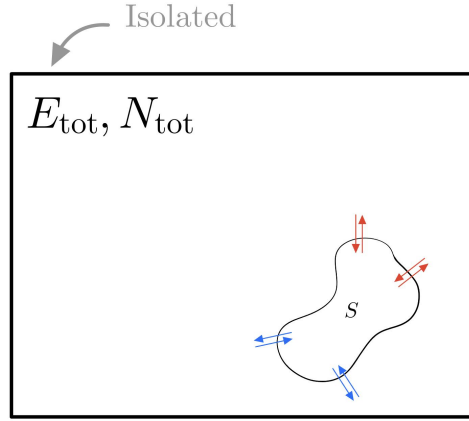


Figure 6: System of interest as a small part of a large, isolated “supersystem”. The energy and particle number in the supersystem are fixed to E_{tot} and N_{tot} respectively. The reduced state of the system can then be shown to be the Gibbs state.

Since our system of interest is part of the supersystem, we may write the Hamiltonian and particle-number operator as

$$\hat{H}_{\text{tot}} = \hat{H}_S + \hat{H}_B + \hat{V}, \quad \hat{N}_{\text{tot}} = \hat{N}_S + \hat{N}_B, \quad (67)$$

where the subscript B stands for “bath” and describes the remainder of the supersystem. We now make a weak coupling approximation that is crucial to obtain the Gibbs state: we assume that \hat{V} is sufficiently weak such that we may neglect the coupling energy and the energy and particle eigenstates of the supersystem approximately factorize

$$|E, N\rangle \simeq |E_S, N_S\rangle \otimes |E_B, N_B\rangle. \quad (68)$$

The density matrix in Eq. (63) may then be written as

$$\hat{\rho}_{\text{tot}} = \sum_{E_S, N_S} \sum_{E_B, N_B} p_{\text{tot}}(E_S + E_B, N_S + N_B) |E_S, N_S\rangle\langle E_S, N_S| \otimes |E_B, N_B\rangle\langle E_B, N_B|. \quad (69)$$

We are interested in the reduced state of the system obtained by taking the partial trace over the bath

$$\hat{\rho}_S = \text{Tr}_B\{\hat{\rho}_{\text{tot}}\} = \sum_{E_B, N_B} \langle E_B, N_B | \hat{\rho}_{\text{tot}} | E_B, N_B \rangle = \sum_{E_S, N_S} p_S(E_S, N_S) |E_S, N_S\rangle\langle E_S, N_S|. \quad (70)$$

The probability for the system to be in a state with energy E_S and particle number N_S may be written as

$$p_S(E_S, N_S) = \sum_{E_B, N_B} p_{\text{tot}}(E_S + E_B, N_S + N_B) = \frac{\Omega_B(E_{\text{tot}} - E_S, N_{\text{tot}} - N_S) \delta E \delta N}{\Omega(E_{\text{tot}}, N_{\text{tot}}) \delta E \delta N}, \quad (71)$$

where the numerator in the last expression denotes the number of states in the bath, i.e., the number of terms in the sum $\sum_{E_B, N_B} p_{\text{tot}}(E_S + E_B, N_S + N_B)$ which are non-vanishing.

In analogy to Eq. (66), the entropy of the bath is given by

$$S_B(E, N) = k_B \ln[\Omega_B(E_{\text{tot}} - E, N_{\text{tot}} - N) \delta E \delta N]. \quad (72)$$

We note that the factor of k_B appears here because this is the thermodynamic, not the von Neumann entropy. Since the system is considered to be small, we may expand the bath entropy around E_{tot} and N_{tot} to obtain

$$\begin{aligned} S_B(E_{\text{tot}} - E_S, N_{\text{tot}} - N_S) &\simeq S_B(E_{\text{tot}}, N_{\text{tot}}) - E_S \partial_E S_B(E, N_{\text{tot}})|_{E=E_{\text{tot}}} \\ &\quad - N_S \partial_N S_B(E_{\text{tot}}, N)|_{N=N_{\text{tot}}} \\ &= S_B(E_{\text{tot}}, N_{\text{tot}}) - \frac{E_S - \mu N_S}{T}, \end{aligned} \quad (73)$$

where we identified $\partial_E S_B(E, N) = 1/T$ and $\partial_N S_B(E, N) = -\mu/T$. Inserting the last expression into Eq. (71) results in

$$p_S(E_S, N_S) = \frac{\Omega_B(E_{\text{tot}}, N_{\text{tot}}) \delta E \delta N}{\Omega(E_{\text{tot}}, N_{\text{tot}}) \delta E \delta N} e^{-\beta(E_S - \mu N_S)} = \frac{e^{-\beta(E_S - \mu N_S)}}{Z}, \quad (74)$$

where the last equality follows from the normalization of the state. Since this is exactly the probability for the Gibbs state given in Eq. (61), we have shown that a small subsystem of a large and closed supersystem is described by the Gibbs state if the supersystem is described by the microcanonical ensemble (i.e., has well defined energy and particle number) and if the system is weakly coupled to the remainder of the supersystem.

II.1.2. Jaynes' maximum entropy principle

The second motivation for the Gibbs state that we discuss is based on Jaynes' maximum entropy principle [29, 30]. The basic idea behind this principle is that an adequate description of the physical system should only encode the information that we actually have. As discussed above, equilibrium states may be described by intensive variables such as temperature and

chemical potential. Equivalently, they may be described by the conjugate extensive quantities provided by the average energy \bar{E} and the average particle number \bar{N} . Following Jaynes', we take \bar{E} and \bar{N} as the prior data, i.e., the knowledge that we have about the state. Jaynes' crucial insight was that in order to avoid encoding any other knowledge in the state, the entropy, a quantifier for lack of knowledge, should be maximized. Mathematically, the Gibbs state is then obtained by maximizing the von Neumann entropy under the constraints

$$\bar{E} = \langle \hat{H} \rangle, \quad \bar{N} = \langle \hat{N} \rangle. \quad (75)$$

To perform this maximization, we start by considering states of the form

$$\hat{\rho} = \sum_n p_n |E_n, N_n\rangle \langle E_n, N_n|, \quad \hat{H} |E_n, N_n\rangle = E_n |E_n, N_n\rangle, \quad \hat{N} |E_n, N_n\rangle = N_n |E_n, N_n\rangle. \quad (76)$$

This form may be motivated by demanding that equilibrium states do not change in time, which implies [see also Eq. (16)]

$$\hat{U}(t) \hat{\rho} \hat{U}^\dagger(t) = 0 \Leftrightarrow [\hat{H}, \hat{\rho}] = 0, \quad (77)$$

and that there are no coherent superpositions of states with different number of particles, which implies $[\hat{N}, \hat{\rho}] = 0$. The latter assumption may be motivated by a particle superselection rule [31] and it does not apply when considering scenarios with a vanishing chemical potential $\mu = 0$. We now want to maximize the von Neumann entropy

$$S_{\text{vN}}(\hat{\rho}) = - \sum_n p_n \ln p_n, \quad (78)$$

under the following three constraints

$$\sum_n p_n = 1, \quad \sum_n p_n E_n = \bar{E}, \quad \sum_n p_n N_n = \bar{N}, \quad (79)$$

where the first constraint simply ensures the normalization of the state. Such constrained maximization problems can be solved by the method of Lagrange multipliers [32]. To this end, we define the function

$$\mathcal{L} = - \sum_n p_n \ln p_n - \lambda_0 \left(\sum_n p_n - 1 \right) - \lambda_1 \left(\sum_n p_n E_n - \bar{E} \right) - \lambda_2 \left(\sum_n p_n N_n - \bar{N} \right). \quad (80)$$

The solution to the maximization procedure is the distribution $\{p_n\}$ that obeys

$$\frac{\partial \mathcal{L}}{\partial p_n} = - \ln p_n - 1 - \lambda_0 - \lambda_1 E_n - \lambda_2 N_n = 0. \quad (81)$$

We now identify

$$\lambda_1 = \beta, \quad \lambda_2 = -\beta\mu, \quad e^{\lambda_0+1} = Z. \quad (82)$$

The solution of Eq. (81) then reads

$$p_n = \frac{e^{-\beta(E_n - \mu N_n)}}{Z}, \quad (83)$$

recovering the Gibbs state given in Eq. (61). The Lagrange multipliers or, equivalently, the quantities β , μ , and Z are fully determined by the constraints given in Eq. (79).

Introducing the *grand potential* which plays a similar role to the free energy

$$\Phi_G = \langle \hat{H} \rangle - k_B T S_{\text{vN}}(\hat{\rho}) - \mu \langle \hat{N} \rangle, \quad (84)$$

we may write Eq. (80) as

$$\mathcal{L} = -\Phi_G - \lambda_0 \left(\sum_n p_n - 1 \right) + (\lambda_1 \bar{E} + \lambda_2 \bar{N}). \quad (85)$$

The last term may be dropped as it does not depend on p_n . The last equation then implies that maximizing the von Neumann entropy given the average energy and average particle number is mathematically equivalent to minimizing the grand potential (the only constraint left ensures the normalization of the state).

II.1.3. Complete passivity

The final motivation we provide for the Gibbs state is based on the notion of *passive states* [33]. These are states from which no work can be extracted. To define passive states, we consider an isolated system that obeys the time-evolution given in Eq. (16). For an isolated system with a time-dependent Hamiltonian, we interpret the total energy change of the system as work. This can be motivated by considering the time-dependence of the Hamiltonian as mediated by a classical field describing a macroscopic degree of freedom. In analogy to a piston compressing a gas, the energy change mediated by this macroscopic degree of freedom should be considered to be work. We now consider a work protocol of duration τ , where the Hamiltonian is changed over time $\hat{H}(t)$ such that

$$\hat{H} \equiv \hat{H}(0) = \hat{H}(\tau). \quad (86)$$

The work extracted during this protocol reads

$$W_{\text{ex}} = \text{Tr}\{\hat{H}\hat{\rho}\} - \text{Tr}\{\hat{H}\hat{U}\hat{\rho}\hat{U}^\dagger\}, \quad (87)$$

where $\hat{\rho}$ denotes the initial state of the system and the unitary $\hat{U} \equiv \hat{U}(\tau)$ is determined by the time-dependent Hamiltonian, see Eq. (16). We note that with a suitable Hamiltonian, any unitary operator can be generated.

A passive state can now be defined as a state τ obeying

$$\text{Tr}\{\hat{H}(\hat{\tau} - \hat{U}\hat{\tau}\hat{U}^\dagger)\} \leq 0 \quad \forall \hat{U}, \quad (88)$$

which implies that no work can be extracted from passive states, no matter how the time-dependent Hamiltonian is designed. Passive states are of the form

$$\hat{\tau} = \sum_n p_n |E_n\rangle\langle E_n|, \quad \text{with} \quad E_0 \leq E_1 \leq E_2 \cdots \quad p_0 \geq p_1 \geq p_2 \cdots \quad (89)$$

Remarkably, taking multiple copies of a passive state may result in a state that is no longer passive. This suggests the definition of *completely passive states* [33]: a state $\hat{\tau}$ is completely passive iff

$$\text{Tr}\{\hat{H}_N(\tau^N - \hat{U}\tau^N\hat{U}^\dagger)\} \leq 0 \quad \forall \hat{U}, \quad (90)$$

where

$$\hat{H}_N = \hat{H} \oplus \hat{H} \oplus \cdots \oplus \hat{H}, \quad \hat{\tau}^N = \hat{\tau} \otimes \hat{\tau} \otimes \cdots \otimes \hat{\tau}. \quad (91)$$

This implies that it is not possible to extract work from completely passive states even if we take multiple copies and let them interact during the work protocol. Remarkably, the only completely passive states are Gibbs states in the canonical ensemble (assuming no degeneracy in the ground state)

$$\hat{\rho}_c = \frac{e^{-\beta \hat{H}}}{\text{Tr}\{e^{-\beta \hat{H}}\}}. \quad (92)$$

In complete analogy, the grand-canonical Gibbs state is completely passive with respect to $\hat{H} - \mu \hat{N}$, i.e., the average $\langle \hat{H} - \mu \hat{N} \rangle$ cannot be lowered by any unitary, even when taking multiple copies. If we further assume a particle-superselection rule [31], preventing the creation of coherent superpositions of different particle numbers as long as $\mu \neq 0$, then the grand-canonical Gibbs state in Eq. (61) is completely passive since $[\hat{U}, \hat{N}] = 0$.

II.2. Equivalence of ensembles in the thermodynamic limit

We have already encountered the grand-canonical, the canonical, as well as the micro-canonical ensemble. Here we discuss these ensembles in a bit more detail and argue that they all become equivalent in the thermodynamic limit, which is the limit of large systems relevant for macroscopic thermodynamics.

Microcanonical ensemble

$$\hat{\rho}_M = \sum_{\substack{\bar{E} \leq E < \bar{E} + \delta E \\ \bar{N} \leq N < \bar{N} + \delta N}} \frac{1}{\Omega(\bar{E}, \bar{N}) \delta E \delta N} |E, N\rangle \langle E, N|, \quad (93)$$

where $\Omega(\bar{E}, \bar{N})$ denotes the density of states that we have encountered in Eq. (65). In the microcanonical ensemble, both the particle number as well as the energy is fixed, where fixed means that all states within an energy (particle number) shell of thickness δE (δN) contribute. Within this shell, the state is assumed to be completely mixed, i.e., all states have equal weight. As such, the state maximizes the von Neumann entropy for fixed \bar{E} and \bar{N} .

Canonical ensemble

$$\hat{\rho}_c = \sum_{\bar{N} \leq N < \bar{N} + \delta N} \sum_E \frac{e^{-\beta E}}{Z_c} |E, N\rangle \langle E, N| = \frac{e^{-\beta \hat{H}_{\bar{N}}}}{\text{Tr}\{e^{-\beta \hat{H}_{\bar{N}}}\}}, \quad (94)$$

where $\hat{H}_{\bar{N}}$ denotes the Hamiltonian projected onto the relevant particle-number subspace

$$\hat{H}_{\bar{N}} = \sum_{\bar{N} \leq N < \bar{N} + \delta N} |N\rangle \langle N| \hat{H} |N\rangle \langle N|, \quad |N\rangle = \sum_E |E, N\rangle. \quad (95)$$

In the canonical ensemble, only the particle number is fixed. The average energy $\langle \hat{H} \rangle$ is determined by the temperature of the surroundings and the canonical ensemble is the adequate equilibrium state when energy (but not particles) can be exchanged with the environment. The canonical Gibbs state maximizes the von Neumann entropy for a fixed particle number \bar{N} and

an average energy given by $\langle \hat{H} \rangle = \bar{E}$. Furthermore, the canonical Gibbs state minimizes the free energy

$$F = \langle \hat{H} \rangle - k_B T S_{\text{vN}}(\hat{\rho}), \quad (96)$$

when the particle number \bar{N} is fixed.

Grand-canonical ensemble The grand-canonical Gibbs is given in Eq. (61). As discussed above, it maximizes the von Neumann entropy for given average values of energy and particle number. This is equivalent to minimizing the grand potential given in Eq. (84). The grand-canonical ensemble is the adequate description when both energy and particles may be exchanged with the environment. The average energy and particle number are then determined by the temperature and chemical potential of the environment respectively.

Thermodynamic limit and equivalence of ensembles The thermodynamic limit is the limit of large systems which formally can be defined as

$$V \rightarrow \infty, \quad \frac{\bar{E}}{V} = \text{cst.}, \quad \frac{\bar{N}}{V} = \text{cst.} \quad (97)$$

This can be achieved by setting $V \propto x$, $\bar{E} \propto x$, $\bar{N} \propto x$, and letting $x \rightarrow \infty$. In the thermodynamic limit, all ensembles become equivalent [34] because relative fluctuations around average values vanish. Here, we illustrate this for the canonical ensemble. In this ensemble, the probability for the system to take on a certain energy obeys

$$p(E) \propto e^{-\beta E} \Omega(E, \bar{N}). \quad (98)$$

As it turns out, this function becomes highly peaked in the thermodynamic limit. This can be seen from the relative fluctuations

$$\frac{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}{\langle \hat{H} \rangle^2} = -\frac{1}{\langle \hat{H} \rangle} \partial_\beta \langle \hat{H} \rangle = \frac{k_B T^2}{\langle \hat{H} \rangle^2} C \propto x, \quad (99)$$

where we introduced the heat capacity

$$C = \partial_T \langle \hat{H} \rangle, \quad (100)$$

which quantifies the change of energy upon a change of temperature. The last equality in Eq. (99) follows because the heat capacity is an extensive quantity and is thus proportional to x for large systems. Equation (99) implies that in the thermodynamic limit, the relative fluctuations vanish. The probability distribution for the system to take on a given relative energy may then be approximated as a Gaussian distribution (see Ref. [21] for a discussion on higher moments)

$$p(E/\bar{E}) \simeq \frac{\bar{E}}{\sqrt{2\pi k_B T^2 C}} e^{-\frac{(E/\bar{E}-1)^2}{2k_B T^2 C/\bar{E}^2}}, \quad (101)$$

which tends to a Dirac delta distribution $\delta(E/\bar{E} - 1)$ in the thermodynamic limit.

III. The laws of thermodynamics

In this section, we discuss how the laws of thermodynamics emerge in a quantum mechanical framework.

III.1. The general scenario

The general scenario we consider consists of a system coupled to multiple baths (or reservoirs) which are in local thermal equilibrium as sketched in Fig. 7. This is described by the Hamiltonian

$$\hat{H}_{\text{tot}}(t) = \hat{H}_S(t) + \sum_{\alpha} \left(\hat{H}_{\alpha} + \hat{V}_{\alpha} \right), \quad (102)$$

where the system is labeled by the subscript S and the baths are labeled by the index α . the term \hat{V}_{α} denotes the coupling between the system and bath α . Because the system and baths together comprise an isolated system, the time evolution of the total density matrix is given by

$$\hat{\rho}_{\text{tot}}(t) = \hat{U}(t) \hat{\rho}_{\text{tot}}(0) \hat{U}^{\dagger}(t) \quad \Leftrightarrow \quad \partial_t \hat{\rho}_{\text{tot}}(t) = -i[\hat{H}_{\text{tot}}(t), \hat{\rho}_{\text{tot}}(t)], \quad (103)$$

where the time-evolution operator is given by

$$\hat{U}(t) = \mathcal{T} e^{-i \int_0^t dt' \hat{H}_{\text{tot}}(t')}, \quad (104)$$

with \mathcal{T} denoting the time-ordering operator (see Sec. I.1.2) and we allow the system Hamiltonian to be time-dependent while we assume the bath Hamiltonians as well as the coupling terms to be time-independent.

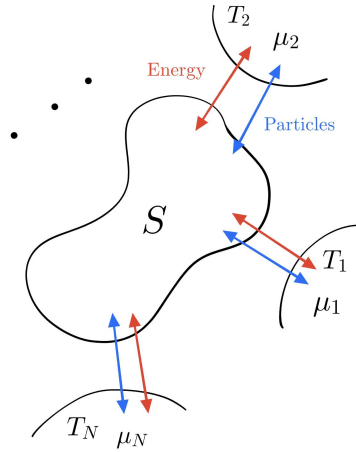


Figure 7: General scenario. A system can exchange both energy and particles with N thermal reservoirs, described by the temperatures T_{α} and the chemical potentials μ_{α} .

As seen in Sec. I.2, the energy flows between the system and the baths are of crucial importance in thermodynamics. This motivates considering the mean energy change of reservoir α

$$\partial_t \langle \hat{H}_{\alpha} \rangle = \text{Tr} \left\{ \hat{H}_{\alpha} \partial_t \hat{\rho}_{\text{tot}} \right\} = \partial_t \langle \hat{H}_{\alpha} - \mu_{\alpha} \hat{N}_{\alpha} \rangle + \mu_{\alpha} \partial_t \langle \hat{N}_{\alpha} \rangle = J_{\alpha} + P_{\alpha}. \quad (105)$$

Here we divided the energy change into a part that we call the heat current J_{α} and a part that we call the power P_{α} that enters reservoir α . Throughout these notes, the sign convention is such that energy flows are positive when flowing toward the body that their index refers to. To motivate the separation of energy flows into heat and work, we introduce the concept of entropy production in the quantum regime.

III.2. Entropy production

The standard extension of the entropy to the quantum regime is the von Neumann entropy. However, under unitary time-evolution, the von Neumann entropy is constant and thus

$$\partial_t S_{vN}[\hat{\rho}_{\text{tot}}] = -\partial_t \text{Tr}\{\hat{\rho}_{\text{tot}}(t) \ln \hat{\rho}_{\text{tot}}(t)\} = 0. \quad (106)$$

The von Neumann entropy of the total system can thus not tell us anything about how energy flows between systems and reservoirs. To make progress, we consider an effective description based on local thermal equilibrium [i.e., the reservoirs are described by the Gibbs state given in Eq. (61)]

- True description: $\hat{\rho}_{\text{tot}}(t)$
- Effective description: $\hat{\rho}_S(t) \otimes_{\alpha} \hat{\tau}_{\alpha}$

where $\hat{\rho}_S = \text{Tr}_B\{\hat{\rho}_{\text{tot}}\}$ and we denote the Gibbs state describing bath α as

$$\hat{\tau}_{\alpha} = \frac{e^{-\beta_{\alpha}(\hat{H}_{\alpha} - \mu_{\alpha}\hat{N}_{\alpha})}}{Z_{\alpha}}. \quad (107)$$

The effective description thus contains all information on the system but neglects any changes to the reservoirs as well as the correlations that may build up between system and reservoirs. Such an effective description is often the best one can do in an experiment, where one might have control over the microscopic degrees of freedom of the system only.

We now consider the quantum relative entropy between the true state $\hat{\rho}_{\text{tot}}(t)$ and our effective description

$$S[\hat{\rho}_{\text{tot}}||\hat{\rho}_S \otimes_{\alpha} \hat{\tau}_{\alpha}] = S_{vN}[\hat{\rho}_S] + \sum_{\alpha} \beta_{\alpha} \langle \hat{H}_{\alpha} - \mu_{\alpha} \hat{N}_{\alpha} \rangle + \sum_{\alpha} \ln Z_{\alpha} - S_{vN}[\hat{\rho}_{\text{tot}}]. \quad (108)$$

As discussed in Sec. I.3, this quantity may be interpreted as the information that is lost due to our effective description. We now introduce the *entropy production rate* [35]

$$\dot{\Sigma} = k_B \partial_t S[\hat{\rho}_{\text{tot}}||\hat{\rho}_S \otimes_{\alpha} \hat{\tau}_{\alpha}] = k_B \partial_t S_{vN}[\hat{\rho}_S] + \sum_{\alpha} \frac{J_{\alpha}}{T_{\alpha}}, \quad (109)$$

where averages are with respect to the total state $\langle \hat{X} \rangle = \text{Tr}\{\hat{X} \hat{\rho}_{\text{tot}}(t)\}$ and we used $\ln \hat{\tau}_{\alpha} = -\beta_{\alpha}(\hat{H}_{\alpha} - \mu_{\alpha}\hat{N}_{\alpha}) - \ln Z_{\alpha}$ as well as $\ln(\hat{A} \otimes \hat{B}) = \ln(\hat{A}) \otimes \mathbb{1} + \mathbb{1} \otimes \ln(\hat{B})$. The entropy production rate can thus be interpreted as the rate at which information is lost by our local equilibrium description, due to the build up of correlations between system and bath as well as changes to the reservoirs. Note that it is not guaranteed to be positive. Finite size effects as well as non-Markovian dynamics can result in a negative entropy production rate (a backflow of information from the bath). However, as we will see later, for infinitely large and memoryless baths, the entropy production rate is ensured to be positive at all times as information is irretrievably lost at all times when one can only access the system alone.

Note that Eq. (109) motivates the interpretation of J_{α} as a heat flow, such that the entropy production associated to bath α is given by the usual expression for baths which remain in thermal equilibrium. Interestingly, we may refine our effective description by using time-dependent temperatures and chemical potentials [36, 37]

$$\tau_{\alpha}(t) = \frac{e^{-\beta_{\alpha}(t)(\hat{H}_{\alpha} - \mu_{\alpha}(t)\hat{N}_{\alpha})}}{Z_{\alpha}}, \quad (110)$$

such that

$$\text{Tr}\{\hat{H}_\alpha \hat{\rho}_{\text{tot}}(t)\} = \text{Tr}\{\hat{H}_\alpha \hat{\tau}_\alpha(t)\}, \quad \text{Tr}\{\hat{N}_\alpha \hat{\rho}_{\text{tot}}(t)\} = \text{Tr}\{\hat{N}_\alpha \hat{\tau}_\alpha(t)\}. \quad (111)$$

In this case, one may show that

$$k_B \partial_t S_{\text{vN}}[\hat{\tau}_\alpha(t)] = \frac{J_\alpha(t)}{T_\alpha(t)}, \quad (112)$$

and the entropy production rate reduces to

$$\begin{aligned} \dot{\Sigma} &= k_B \partial_t S[\hat{\rho}_{\text{tot}} || \hat{\rho}_S \otimes_\alpha \hat{\tau}_\alpha(t)] = k_B \partial_t S_{\text{vN}}[\hat{\rho}_S] + k_B \sum_\alpha \partial_t S_{\text{vN}}[\hat{\tau}_\alpha(t)] \\ &= k_B \partial_t S_{\text{vN}}[\hat{\rho}_S] + \sum_\alpha \frac{J_\alpha(t)}{T_\alpha(t)}. \end{aligned} \quad (113)$$

III.3. The first law of thermodynamics

To derive the first law of thermodynamics, we consider the change in the average energy of system and baths

$$\begin{aligned} \partial_t \langle \hat{H}_{\text{tot}}(t) \rangle &= \text{Tr} \left\{ [\partial_t \hat{H}_{\text{tot}}(t)] \hat{\rho}_{\text{tot}} \right\} + \text{Tr} \left\{ \hat{H}_{\text{tot}}(t) \partial_t \hat{\rho}_{\text{tot}} \right\} \\ &= \partial_t \langle \hat{H}_S(t) \rangle + \partial_t \sum_\alpha \langle \hat{H}_\alpha \rangle + \partial_t \sum_\alpha \langle \hat{V}_\alpha \rangle. \end{aligned} \quad (114)$$

Using Eq. (66), the last term on the first line can be shown to vanish. With the help of the last equation and Eq. (105), we may then derive the first law of thermodynamics (note that the energy flows are defined to be positive when they enter the location corresponding to their index)

$$\partial_t \langle \hat{H}_S(t) \rangle = P_S(t) - \sum_\alpha [J_\alpha(t) + P_\alpha(t)] - \partial_t \sum_\alpha \langle \hat{V}_\alpha \rangle, \quad P_S \equiv \langle \partial_t \hat{H}_S \rangle, \quad (115)$$

where P_S denotes the power entering the system due to some external classical drive that renders \hat{H}_S time-dependent. The term due to the coupling energy $\langle \hat{V}_\alpha \rangle$ can be neglected when the coupling is weak, which is a common assumption for open quantum systems. Relaxing this assumption and considering the thermodynamics of systems that are strongly coupled to the environment is an exciting ongoing avenue of research [38–41].

III.4. The second law of thermodynamics

Let us consider an initial state which is a product state of the form

$$\hat{\rho}_{\text{tot}}(0) = \hat{\rho}_S(0) \otimes_\alpha \hat{\tau}_\alpha. \quad (116)$$

In this case, Eq. (108) can be written as

$$\Sigma \equiv k_B S[\hat{\rho}_{\text{tot}}(t) || \hat{\rho}_S(t) \otimes_\alpha \hat{\tau}_\alpha] = k_B S_{\text{vN}}[\hat{\rho}_S(t)] - k_B S_{\text{vN}}[\hat{\rho}_S(0)] + \sum_\alpha \frac{Q_\alpha}{T_\alpha}, \quad (117)$$

where the heat is defined as

$$Q_\alpha = \text{Tr} \left\{ (\hat{H}_\alpha - \mu_\alpha \hat{N}_\alpha) \hat{\rho}_{\text{tot}}(t) \right\} - \text{Tr} \left\{ (\hat{H}_\alpha - \mu_\alpha \hat{N}_\alpha) \hat{\rho}_{\text{tot}}(0) \right\}, \quad (118)$$

and we used that $S[\hat{\rho}_{\text{tot}}(0) || \hat{\rho}_S(0) \otimes_\alpha \hat{\tau}_\alpha] = 0$. Since it is expressed as a quantum relative entropy, we have

$$\Sigma \geq 0. \quad (119)$$

From an information point of view, this inequality tells us that if our effective description is true at $t = 0$, then it can only be worse at later times. As mentioned above, the entropy production rate $\dot{\Sigma}$ is not always guaranteed to be positive (i.e., Σ is not necessarily a monotonously increasing function of time). However, at small times, Eq. (119) ensures that the entropy production rate is also positive. We note that with a time-dependent effective description, see Eq. (110), Eqs. (117) and (119) still hold.

The above description relies on Eq. (116), i.e., on the fact that at some time that we call $t = 0$, the system and the reservoirs are uncorrelated and the reservoirs truly are in a thermal state. Let us now consider the family of states

$$\hat{\rho}_{\text{tot}}^{t_0}(t_0) = \hat{\rho}_S(t_0) \bigotimes_\alpha \hat{\tau}_\alpha. \quad (120)$$

We can choose each of these states as the initial condition for the time-evolution of the total density matrix. However, the reduced state of the system might depend on the chosen t_0

$$\hat{\rho}_S^{t_0}(t) = \text{Tr}_B \{ \hat{\rho}_{\text{tot}}^{t_0}(t) \} = \text{Tr}_B \{ \hat{U}(t, t_0) \hat{\rho}_{\text{tot}}^{t_0}(t_0) \hat{U}^\dagger(t, t_0) \}. \quad (121)$$

Note that since Eq. (120) provides the initial condition, we only consider times $t \geq t_0$.

If $\dot{\Sigma}$ is independent of our choice of t_0 , then it can be shown that $\dot{\Sigma} \geq 0$ at all times since

$$\begin{aligned} \dot{\Sigma}(t) &\simeq \frac{S[\hat{\rho}_{\text{tot}}^{t_0}(t) || \hat{\rho}_S^{t_0}(t) \otimes_\alpha \hat{\tau}_\alpha] - S[\hat{\rho}_{\text{tot}}^{t_0}(t - dt) || \hat{\rho}_S^{t_0}(t - dt) \otimes_\alpha \hat{\tau}_\alpha]}{dt} \\ &= \frac{S[\hat{\rho}_{\text{tot}}^t(t_0 + dt) || \hat{\rho}_S^t(t_0 + dt) \otimes_\alpha \hat{\tau}_\alpha]}{dt} \geq 0, \end{aligned} \quad (122)$$

where we have chosen $t = t_0 + dt$ in the second line.

As we will see in the next section, in the limit of infinitely large and memory-less reservoirs which couple weakly to the system, no observables depend on the time t_0 at which we assume system and reservoirs to be uncorrelated. This ensures that for *classical* reservoirs, the entropy production rate is positive at all times and suggests the following picture: In reality, the state never truly factorizes as in Eq. (120). However, at all times it is very close to it. At all times, we can thus assume it to be of the form given in Eq. (120). However, once we fix the state to be of this form for a given time, we also need to allow for (small) deviations of this form to compute the entropy production according to Eq. (109).

III.5. The zeroth law of thermodynamics

For completeness, we will also briefly mention the zeroth and the third law of thermodynamics, although they will play a less important role throughout these notes. The zeroth law is usually phrased as: *If two systems are both in equilibrium with a third one, then they are in equilibrium with each other.* Being equipped with definitions for temperature and chemical potential, then

the zeroth law implies: *Systems in equilibrium with each other have the same temperature and chemical potential.*

When a small system is coupled to a large equilibrium bath, then the reduced system state is expected to tend to [41]

$$\lim_{t \rightarrow \infty} \hat{\rho}_S(t) = \frac{\text{Tr}_B \left\{ e^{-\beta(\hat{H}_{\text{tot}} - \mu \hat{N}_{\text{tot}})} \right\}}{\text{Tr} \left\{ e^{-\beta(\hat{H}_{\text{tot}} - \mu \hat{N}_{\text{tot}})} \right\}} \xrightarrow[\text{coupling}]{\text{weak}} \frac{e^{\beta(\hat{H}_S - \mu \hat{N}_S)}}{Z}. \quad (123)$$

As expected, in equilibrium, the system is thus characterized by the same temperature and chemical potential as the bath. We note that equilibrium may only be reached if \hat{H}_{tot} is time-independent and if there is only a single temperature and a single chemical potential characterizing the environment. The exact range of validity of the first equality in Eq. (123) is a subject of ongoing research and there are many fascinating open questions at strong coupling [41].

III.6. The third law of thermodynamics

The formulation of the third law of thermodynamics that we consider here is known as Nernst's unattainability principle [42]. In its modern formulation, it reads: *It is impossible to cool a system to its ground state (or create a pure state) without diverging resources.* These resources may be time, energy (in the form of work), or control complexity [43]. When a diverging amount of work is available, one may cool a system to the ground state by increasing the energy of all excited states by an infinite amount. Then, the equilibrium state at any finite temperature reduces to the ground state which can thus be obtained by equilibration with any thermal reservoir. When an infinite amount of time is available, this process may be performed reversibly, reducing the work cost to a finite amount. Loosely speaking, infinite control complexity allows one to parallelize this cooling process and reach the ground state using only a finite amount of time and work [43].

Existing proofs of the third law of thermodynamics for quantum systems [43, 44] use the framework of the resource theory of thermodynamics [13] and are not directly applicable to the scenario considered in these notes.

IV. Markovian master equations

In this section, we consider Markovian master equations as a description for the reduced state of the system $\hat{\rho}_S$. Markovianity implies that no memory effects of the bath are taken into account. For instance, a particle that is emitted from the system will not be reabsorbed by the system before losing all memory of the emission event. In principle, memory effects are always present but if the coupling between system and bath is weak, these effects can often safely be ignored. There are numerous references that discuss Markovian master equations going substantially beyond these notes, see for instance Refs. [45–48]

As illustrated in Fig. 8, the time-evolution of the reduced density matrix can be described by a *universal dynamical map* (UDM). A UDM \mathcal{E} is a linear map which transforms a density matrix into another density matrix. Furthermore, it is independent of the density matrix it acts upon. In its most general form, a UDM can be written as

$$\mathcal{E}\hat{\rho} = \sum_j \hat{K}_j \hat{\rho} \hat{K}_j^\dagger, \quad \sum_j \hat{K}_j^\dagger \hat{K}_j = \mathbb{1},$$

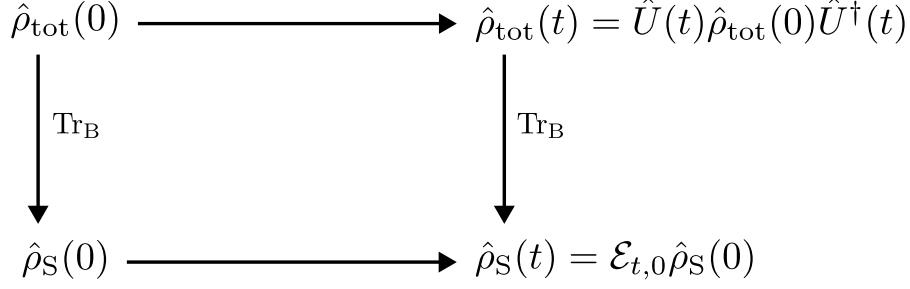


Figure 8: Time evolution of total and reduced density matrices. The total density matrix evolves unitarily, according to Eq. (103). The reduced density matrix at time t can either be obtained by tracing out the environment from $\hat{\rho}_{\text{tot}}(t)$, or by evolving $\hat{\rho}_S(0)$ by the universal dynamical map $\mathcal{E}_{t,0}$

where the operators \hat{K}_j are called Kraus operators.

We say that a system obeys Markovian time-evolution if it is described by a *divisible* UDM, i.e.,

$$\hat{\rho}(t) = \mathcal{E}_{t,t_0}\hat{\rho} = \mathcal{E}_{t,t_1}\mathcal{E}_{t_1,t_0}\hat{\rho},$$

For any intermediate time $t_0 < t_1 < t$. Furthermore, we note that a differential equation is a Markovian master equation (i.e., results in Markovian time-evolution of a density matrix) if and only if it can be written in the form

$$\begin{aligned} \partial_t \hat{\rho}(t) &= -i[\hat{H}(t), \hat{\rho}(t)] + \sum_k \gamma_k(t) \left[\hat{L}_k(t) \hat{\rho}(t) \hat{L}_k^\dagger(t) - \frac{1}{2} \{ \hat{L}_k^\dagger(t) \hat{L}_k(t), \hat{\rho}(t) \} \right] \\ &= -i[\hat{H}(t), \hat{\rho}(t)] + \sum_k \gamma_k(t) \mathcal{D}[\hat{L}_k(t)] \hat{\rho}(t), \end{aligned} \quad (124)$$

where $\hat{H}(t)$ is Hermitian, $\gamma_k(t) \geq 0$, and the operators \hat{L}_k are referred to as Lindblad jump operators. For a proof, see Ref. [46]. This form of the master equation is also called GKLS form, after Gorini, Kosakowski, Sudarshan [49], and Linblad [50] who considered the time-independent case. In the rest of this chapter, we provide detailed derivations for Markovian master equations that describe our general scenario introduced in Sec. III.1.

IV.1. Nakajima-Zwanzig superoperators

To derive Markovian master equations, we use the Nakajima-Zwanzig projection operator approach [51, 52] following Ref. [53]. To this end, we introduce the superoperators

$$\mathcal{P}\hat{\rho}_{\text{tot}} = \text{Tr}_B \{ \hat{\rho}_{\text{tot}} \} \bigotimes_{\alpha} \hat{\tau}_{\alpha} = \hat{\rho}_S \bigotimes_{\alpha} \hat{\tau}_{\alpha}, \quad \mathcal{Q} = 1 - \mathcal{P}. \quad (125)$$

Note that these are projectors as $\mathcal{P}^2 = \mathcal{P}$. Further, note that we are interested in the time-evolution of $\mathcal{P}\hat{\rho}_{\text{tot}}(t)$, which provides us with an effective description of the form discussed in Sec. III.2. We consider the general scenario discussed in Sec. III.1, i.e., the Hamiltonian is given by Eq. (102), but we move to an interaction picture (which we denote by a tilde instead of a hat)

$$\tilde{\rho}_{\text{tot}}(t) = \hat{U}_0^\dagger(t) \hat{\rho}_{\text{tot}}(t) \hat{U}_0(t), \quad (126)$$

determined by the unitary operator

$$\hat{U}_0(t) = \mathcal{T} e^{-i \int_0^t dt' [\hat{H}_S(t') + \sum_\alpha \hat{H}_\alpha]}, \quad (127)$$

with \mathcal{T} denoting time-ordering. In the interaction picture, the time-evolution of the total density matrix is determined by

$$\partial_t \tilde{\rho}_{\text{tot}}(t) = -i \sum_\alpha [\tilde{V}_\alpha(t), \tilde{\rho}_{\text{tot}}(t)] = \mathcal{V}(t) \tilde{\rho}_{\text{tot}}(t), \quad (128)$$

where we used Eq. (103) as well as

$$\partial_t \hat{V}(t) = -i \left[\hat{H}_S(t) + \sum_\alpha \hat{H}_\alpha \right] \hat{V}(t), \quad \partial_t \hat{V}^\dagger(t) = i \hat{V}^\dagger(t) \left[\hat{H}_S(t) + \sum_\alpha \hat{H}_\alpha \right], \quad (129)$$

and the coupling Hamiltonian in the interaction picture is given by $\tilde{V}_\alpha(t) = \hat{U}_0^\dagger(t) \hat{V}_\alpha \hat{U}_0(t)$, in analogy to Eq. (126). Finally, we have expressed the commutator in Eq. (128) with the help of the superoperator \mathcal{V} . In the following, we will assume $\mathcal{P}\mathcal{V}(t)\mathcal{P} = 0$. This is not a restriction as it can always be ensured by adding some terms to \hat{H}_S and subtracting them from \hat{V}_α , as we will see below. We can then write

$$\begin{aligned} \partial_t \mathcal{P} \tilde{\rho}_{\text{tot}}(t) &= \mathcal{P}\mathcal{V}(t) \tilde{\rho}_{\text{tot}}(t) = \mathcal{P}\mathcal{V}(t) \mathcal{Q} \tilde{\rho}_{\text{tot}}(t), \\ \partial_t \mathcal{Q} \tilde{\rho}_{\text{tot}}(t) &= \mathcal{Q}\mathcal{V}(t) \tilde{\rho}_{\text{tot}}(t) = \mathcal{Q}\mathcal{V}(t) \mathcal{P} \tilde{\rho}_{\text{tot}}(t) + \mathcal{Q}\mathcal{V}(t) \mathcal{Q} \tilde{\rho}_{\text{tot}}(t), \end{aligned} \quad (130)$$

where we used $\mathcal{P} + \mathcal{Q} = 1$. The formal solution to the second equation is given by

$$\mathcal{Q} \tilde{\rho}_{\text{tot}}(t) = \mathcal{G}(t, 0) \mathcal{Q} \tilde{\rho}_{\text{tot}}(0) + \int_0^t ds \mathcal{G}(t, s) \mathcal{Q}\mathcal{V}(s) \mathcal{P} \tilde{\rho}_{\text{tot}}(s), \quad (131)$$

where we introduced the propagator

$$\mathcal{G}(t, s) = \mathcal{T} e^{\int_s^t \mathcal{Q}\mathcal{V}(\tau) d\tau}. \quad (132)$$

We now assume factorizing initial conditions

$$\tilde{\rho}_{\text{tot}}(0) = \hat{\rho}_S(0) \bigotimes_\alpha \hat{\tau}_\alpha, \quad (133)$$

such that $\mathcal{P} \tilde{\rho}_{\text{tot}}(0) = \tilde{\rho}_{\text{tot}}(0)$ and $\mathcal{Q} \tilde{\rho}_{\text{tot}}(0) = 0$. Inserting Eq. (131) into Eq. (130), we find

$$\partial_t \mathcal{P} \tilde{\rho}_{\text{tot}}(t) = \int_0^t ds \mathcal{P}\mathcal{V}(t) \mathcal{G}(t, s) \mathcal{Q}\mathcal{V}(s) \mathcal{P} \tilde{\rho}_{\text{tot}}(s). \quad (134)$$

We note that this expression is still exact (for the given initial conditions). Since it explicitly depends on $\mathcal{P} \tilde{\rho}_{\text{tot}}$ at previous time, it contains memory effects and does not constitute a Markovian master equation.

IV.2. Born-Markov approximations

We now make a weak coupling approximation. If the coupling between system and baths are proportional to $\hat{V}_\alpha \propto r$, with $r \ll 1$, the propagator in Eq. (132) obeys $\mathcal{G}(t, s) = 1 + \mathcal{O}(r)$ in

$$\partial_t \mathcal{P} \tilde{\rho}_{\text{tot}}(t) = \mathcal{P} \int_0^t ds \mathcal{V}(t) \mathcal{V}(s) \mathcal{P} \tilde{\rho}_{\text{tot}}(s) + \mathcal{O}(r^3), \quad (135)$$

where we again used $\mathcal{P} \mathcal{V}(t) \mathcal{P} = 0$. The last equation implies

$$\partial_t \tilde{\rho}_S(t) = - \int_0^t ds \sum_\alpha \text{Tr}_B \left\{ \left[\tilde{V}_\alpha(t), \left[\tilde{V}_\alpha(t-s), \tilde{\rho}_S(t-s) \otimes_\alpha \hat{\tau}_\alpha \right] \right] \right\}, \quad (136)$$

where we substituted $s \rightarrow t-s$ and we made use of $\text{Tr}_B \{ \tilde{V}_\delta(t) \tilde{V}_\gamma(s) \tilde{\rho}_S(s) \otimes_\alpha \hat{\tau}_\alpha \} = 0$ for $\delta \neq \gamma$. This is similar to the assumption $\mathcal{P} \mathcal{V}(t) \mathcal{P} = 0$ and can always be ensured by an appropriate redefinition of the terms in the Hamiltonian as shown below. We note that Eq. (136) is often obtained by assuming that $\tilde{\rho}_{\text{tot}}(t) = \tilde{\rho}_S(t) \otimes_\alpha \hat{\tau}_\alpha$ at all times, the so-called Born approximation. Here we do not make such an assumption. In agreement with the discussion in the previous section, we consider $\tilde{\rho}_S(t) \otimes_\alpha \hat{\tau}_\alpha$ to be an effective description, which only keeps track of the degrees of the system and neglects changes in the bath state as well as correlations between system and bath.

In addition to the weak coupling approximation, we now make a Markov approximation. To this end, we assume that the integrand in Eq. (136) decreases on a time-scale τ_B (the bath-correlation time, more on this below). If this time-scale is short enough, which is the case for large, memory-less baths, we can assume $\tilde{\rho}_S(t-s)$ to approximately remain constant and replace its time-argument in Eq. (136) by t . Furthermore, using the same argumentation, we can extend the integral to infinity obtaining

$$\partial_t \tilde{\rho}_S(t) = - \int_0^\infty ds \sum_\alpha \text{Tr}_B \left\{ \left[\tilde{V}_\alpha(t), \left[\tilde{V}_\alpha(t-s), \tilde{\rho}_S(t) \otimes_\alpha \hat{\tau}_\alpha \right] \right] \right\}. \quad (137)$$

This equation is Markovian, i.e., it is local in time and does not depend explicitly on the initial conditions. However, it is not in GKLS form and does not in general preserve the positivity of the density matrix, i.e., eigenvalues may become negative. The approximations that result in Eq. (137) are usually called the *Born-Markov* approximations. For a more formal application of these approximations, see Refs. [54, 55]. Note that under the Born-Markov approximations, the effect induced by different baths is additive.

To make progress, we write the coupling Hamiltonian in the general form

$$\hat{V}_\alpha = \sum_k \hat{S}_{\alpha,k} \otimes \hat{B}_{\alpha,k} = \sum_k \hat{S}_{\alpha,k}^\dagger \otimes \hat{B}_{\alpha,k}^\dagger, \quad (138)$$

where we used the Hermiticity of \hat{V}_α in the second equality. We note that the operators $\hat{S}_{\alpha,k}$ and $\hat{B}_{\alpha,k}$ are not necessarily Hermitian. Inserting Eq. (138) into Eq. (137), we find after some algebra

$$\begin{aligned} \partial_t \tilde{\rho}_S(t) = \sum_\alpha \sum_{k,k'} \int_0^\infty ds \left\{ C_{k,k'}^\alpha(s) \left[\tilde{S}_{\alpha,k'}(t-s) \tilde{\rho}_S(t) \tilde{S}_{\alpha,k}^\dagger(t) - \tilde{S}_{\alpha,k}^\dagger(t) \tilde{S}_{\alpha,k'}(t-s) \tilde{\rho}_S(t) \right] \right. \\ \left. + C_{k,k'}^\alpha(-s) \left[\tilde{S}_{\alpha,k'}(t) \tilde{\rho}_S(t) \tilde{S}_{\alpha,k}^\dagger(t-s) - \tilde{\rho}_S(t) \tilde{S}_{\alpha,k}^\dagger(t-s) \tilde{S}_{\alpha,k'}(t) \right] \right\}, \end{aligned} \quad (139)$$

where we introduced the bath correlation functions

$$C_{k,k'}^\alpha(s) = \text{Tr} \left\{ \tilde{B}_{\alpha,k}^\dagger(s) \hat{B}_{\alpha,k'} \hat{\tau}_\alpha \right\}, \quad (140)$$

and we used $[C_{k,k'}^\alpha(s)]^* = C_{k',k}^\alpha(-s)$. These bath correlation functions are usually peaked around $s = 0$ and decay over the time-scale τ_B (indeed, this is how τ_B is defined). If this time-scale is short, the integrand in Eq. (139) decays quickly and the Markov assumption performed above is justified. Note that it is important that this approximation is made in the interaction picture, where $\tilde{\rho}_S$ varies slowly (in the Schrödinger picture, $\hat{\rho}_S$ tends to oscillate with frequencies given by the differences of the eigenvalues of \hat{H}_S).

While Eq. (139) is in general still not in GKLS form, it happens to reduce to GKLS form when $C_{k,k'}^\alpha(s) \propto \delta_{k,k'}$ and

$$[\hat{S}_{\alpha,k}, \hat{H}_S] = \omega_{\alpha,k} \hat{S}_{\alpha,k} \quad \tilde{S}_{\alpha,k}(t) = e^{-i\omega_{\alpha,k}t} \hat{S}_{\alpha,k}, \quad (141)$$

which implies that $\hat{S}_{\alpha,k}$ are ladder operators for the Hamiltonian \hat{H}_S , removing the energy $\omega_{\alpha,k}$ from the system. Before we consider such an example in detail, we briefly justify two assumptions made in the derivation above. To this end, we note that if

$$\text{Tr} \left\{ \hat{B}_{\alpha,k} \hat{\tau}_\alpha \right\} = 0, \quad (142)$$

then it is straightforward to show that

$$\mathcal{P}\mathcal{V}(t)\mathcal{P} = 0, \quad \text{Tr} \left\{ \tilde{V}_\delta(t) \tilde{V}_\gamma(s) \tilde{\rho}_S(t) \otimes_\alpha \hat{\tau}_\alpha \right\} = 0. \quad (143)$$

In case Eq. (142) is not true, we may define

$$\hat{B}'_{\alpha,k} = \hat{B}_{\alpha,k} - \text{Tr} \left\{ \hat{B}_{\alpha,k} \hat{\tau}_\alpha \right\}, \quad (144)$$

which do fulfill $\text{Tr} \left\{ \hat{B}'_{\alpha,k} \hat{\tau}_\alpha \right\} = 0$. Defining

$$\hat{V}'_\alpha = \sum_k \hat{S}_{\alpha,k} \otimes \hat{B}'_{\alpha,k}, \quad \hat{H}'_S(t) = H_S(t) + \sum_{\alpha,k} \text{Tr} \left\{ \hat{B}_{\alpha,k} \hat{\tau}_\alpha \right\} \hat{S}_{\alpha,k}, \quad (145)$$

we have $\hat{H}_{\text{tot}}(t) = H'_S(t) + \sum_\alpha (\hat{H}_\alpha + \hat{V}'_\alpha)$, i.e., the same total Hamiltonian but now in a form such that Eq. (142) holds, ensuring our assumptions given in Eq. (143).

IV.3. Example: equilibration of a quantum dot

We now consider an example provided by a spinless, single-level quantum dot tunnel-coupled to a single fermionic bath. In this case, Eq. (139) happens to already be in GKLS form. The Hamiltonian of system and bath is then given by

$$\hat{H}_{\text{tot}} = \hat{H}_S + \hat{H}_B + \hat{V}, \quad (146)$$

with

$$\hat{H}_S = \varepsilon_d \hat{d}^\dagger \hat{d}, \quad \hat{H}_B = \sum_q \varepsilon_q \hat{c}_q^\dagger \hat{c}_q, \quad \hat{V} = \sum_q \left(g_q \hat{d} \hat{c}_q^\dagger - g_q^* \hat{d}^\dagger \hat{c}_q \right). \quad (147)$$

Here the bath is modeled as a collection of non-interacting fermions and the coupling Hamiltonian describes tunneling of single electrons between the system and the bath (the minus sign arises from the fermionic anti-commutation relations).

We note that for fermions, there is no tensor product structure because operators on the bath and on the system may *anti*-commute. Strictly speaking, the derivation in the last section is thus not valid. However, using a Jordan-Wigner transform, one can map the fermionic system onto a spin system where such a tensor-product structure is provided [47]. After tracing out the bath, the spin operators can then be replaced by fermionic operators again. For the tunneling Hamiltonian that we often use to describe the system-bath coupling for fermions, this procedure is equivalent to replacing the tensor product by the usual product between fermionic operators in the derivation.

IV.3.1. The master equation

Comparing the coupling Hamiltonian to Eq. (138), we may write $\hat{V} = \hat{S}_0 \hat{B}_0 + \hat{S}_1 \hat{B}_1$ with

$$\hat{S}_0 = \hat{d}, \quad \hat{S}_1 = \hat{d}^\dagger, \quad \hat{B}_0 = \sum_q g_q \hat{c}_q^\dagger, \quad \hat{B}_1 = - \sum_q g_q^* \hat{c}_q. \quad (148)$$

We further find

$$[\hat{d}, \hat{H}_S] = \varepsilon_d \hat{d} \quad \Rightarrow \quad \tilde{S}_0(t) = e^{-i\varepsilon_d t} \hat{d}, \quad \tilde{S}_1(t) = e^{i\varepsilon_d t} \hat{d}^\dagger = \tilde{S}_0^\dagger(t), \quad (149)$$

and similarly

$$\tilde{B}_0(t) = \sum_q g_q e^{i\varepsilon_q t} \hat{c}_q^\dagger, \quad \tilde{B}_1(t) = - \sum_q g_q^* e^{-i\varepsilon_q t} \hat{c}_q. \quad (150)$$

These expressions result in the bath correlation functions

$$\begin{aligned} C_{0,0}(s) &= \sum_q |g_q|^2 e^{-i\varepsilon_q s} \text{Tr} \left\{ \hat{c}_q \hat{c}_q^\dagger \hat{\tau}_B \right\} = \sum_q |g_q|^2 e^{-i\varepsilon_q s} [1 - n_F(\varepsilon_q)] \\ &= \int_{-\infty}^{\infty} d\omega e^{-i\omega s} \rho(\omega) [1 - n_F(\omega)], \\ C_{1,1}(s) &= \sum_q |g_q|^2 e^{i\varepsilon_q s} \text{Tr} \left\{ \hat{c}_q^\dagger \hat{c}_q \hat{\tau}_B \right\} = \sum_q |g_q|^2 e^{i\varepsilon_q s} n_F(\varepsilon_q) \\ &= \int_{-\infty}^{\infty} d\omega e^{i\omega s} \rho(\omega) n_F(\omega), \end{aligned} \quad (151)$$

where we introduced the Fermi-Dirac distribution

$$n_F(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}} + 1}, \quad (152)$$

and made use of $\text{Tr}\{\hat{c}_q^\dagger \hat{c}_{q'} \hat{\tau}_B\} = 0$ for $q \neq q'$. Furthermore, it is easy to show that $C_{0,1}(s) = C_{1,0}(s) = 0$ since $\text{Tr}\{(\hat{c}_q^\dagger)^2 \hat{\tau}_B\} = \text{Tr}\{(\hat{c}_q)^2 \hat{\tau}_B\} = 0$. Finally, in the last equalities we introduced the spectral density

$$\rho(\omega) = \sum_q |g_q|^2 \delta(\varepsilon_q - \omega), \quad (153)$$

which can be treated as a continuous function in the limit of a large bath with many modes.

Using Eq. (149), we may re-write the master equation in Eq. (139) as

$$\begin{aligned} \partial_t \tilde{\rho}_S(t) = & \int_{-\infty}^{\infty} ds \left\{ C_{0,0}(s) e^{i\varepsilon_d s} \mathcal{D}[\hat{d}] \tilde{\rho}_S(t) + C_{1,1}(s) e^{-i\varepsilon_d s} \mathcal{D}[\hat{d}^\dagger] \tilde{\rho}_S(t) \right\} \\ & - \frac{1}{2} \int_{-\infty}^{\infty} ds \text{sign}(s) [C_{0,0}(s) e^{i\varepsilon_d s} - C_{1,1}(s) e^{-i\varepsilon_d s}] [\hat{d}^\dagger \hat{d}, \tilde{\rho}_S(t)], \end{aligned} \quad (154)$$

where

$$\mathcal{D}[\hat{A}] \hat{\rho} = \hat{A} \hat{\rho} \hat{A}^\dagger - \frac{1}{2} \{ \hat{A}^\dagger \hat{A}, \hat{\rho} \}. \quad (155)$$

With the help of the bath correlation functions given in Eq. (151), we may evaluate the integrals over s to find the transition rates

$$\begin{aligned} \int_{-\infty}^{\infty} ds C_{0,0}(s) e^{i\varepsilon_d s} &= \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} ds e^{-i(\omega - \varepsilon_d)s} \rho(\omega) [1 - n_F(\omega)] = \kappa [1 - n_F(\varepsilon_d)], \\ \int_{-\infty}^{\infty} ds C_{1,1}(s) e^{-i\varepsilon_d s} &= \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} ds e^{i(\omega - \varepsilon_d)s} \rho(\omega) n_F(\omega) = \kappa n_F(\varepsilon_d), \end{aligned} \quad (156)$$

where we used

$$\int_{-\infty}^{\infty} ds e^{-i(\omega - \varepsilon_d)s} = 2\pi \delta(\omega - \varepsilon_d), \quad (157)$$

and introduced $\kappa \equiv 2\pi \rho(\varepsilon_d)$.

We furthermore find the so-called Lamb shift

$$\begin{aligned} & - \frac{1}{2} \int_{-\infty}^{\infty} ds \text{sign}(s) [C_{0,0}(s) e^{i\varepsilon_d s} - C_{1,1}(s) e^{-i\varepsilon_d s}] \\ &= -i \text{Im} \int_0^{\infty} ds [C_{0,0}(s) e^{i\varepsilon_d s} - C_{1,1}(s) e^{-i\varepsilon_d s}] = iP \int_{-\infty}^{\infty} d\omega \frac{\rho(\omega)}{\omega - \varepsilon_d}, \end{aligned} \quad (158)$$

where we made use of $C_{j,j}^*(s) = C_{j,j}(-s)$ as well as the identity

$$\lim_{t \rightarrow \infty} \int_0^t ds e^{i\omega s} = \pi \delta(\omega) + iP \left(\frac{1}{\omega} \right), \quad (159)$$

with P denoting the Cauchy principal value [i.e., $P(1/\omega)$ is equal to $1/\omega$ except at $\omega = 0$, where the principal value vanishes].

Finally, inserting Eqs. (156) and (158) back into Eq. (154), we find the Markovian master equation in the Schrödinger picture

$$\begin{aligned} \partial_t \hat{\rho}_S(t) &= -i[\hat{H}_S, \hat{\rho}_S(t)] + e^{-i\hat{H}_S t} [\partial_t \tilde{\rho}_S(t)] e^{i\hat{H}_S t} \\ &= -i[\bar{\varepsilon}_d \hat{d}^\dagger \hat{d}, \hat{\rho}_S(t)] + \kappa [1 - n_F(\varepsilon_d)] \mathcal{D}[\hat{d}] \hat{\rho}_S(t) + \kappa n_F(\varepsilon_d) \mathcal{D}[\hat{d}^\dagger] \hat{\rho}_S(t), \end{aligned} \quad (160)$$

where the renormalized dot energy reads

$$\bar{\varepsilon}_d = \varepsilon_d + P \int_{-\infty}^{\infty} d\omega \frac{\rho(\omega)}{\varepsilon_d - \omega}. \quad (161)$$

The bath thus has two effects: Through the dissipative part of the master equations, it describes electrons entering ($\mathcal{D}[\hat{d}^\dagger]$) and leaving ($\mathcal{D}[\hat{d}]$) the quantum dot. Note that to enter the dot, electrons in the bath have to be available, corresponding to the factor n_F while to

leave the dot, empty states have to be available corresponding to the factor $1 - n_F$. In addition, the energy level of the quantum dot is renormalized.

Note that when taking the ratio between the rates of entering and leaving the quantum dot, we obtain the Boltzmann factor

$$e^{\beta(\varepsilon_d - \mu)} = \frac{\kappa[1 - n_F(\varepsilon_d)]}{\kappa n_F(\varepsilon_d)}. \quad (162)$$

This condition is known as *local detailed balance* and it generally holds for transition rates that are induced by reservoirs in thermal equilibrium. It ensures that in equilibrium, the system state tends to a Gibbs state, see also Eq. (168) below.

As discussed above, the Markovian approximation is justified if the bath correlation functions decay on a time scale which is much faster than the time over which $\tilde{\rho}_S$ varies. In the limiting case where both $\rho(\omega)$ as well as $n_F(\omega)$ are independent of ω , the bath correlation functions become proportional to a Dirac delta function and the bath becomes truly *memoryless* (i.e., $\tau_B \rightarrow 0$). In practice, it is sufficient for τ_B to be much shorter than any relevant time-scale of the system. In energy, this translates to the condition that the functions $\rho(\omega)$ as well as $n_F(\omega)$ are flat around the relevant energies of the system. For the present system $\tilde{\rho}_S$ changes on the time-scale $1/\kappa$. The Markov approximation is then valid as long as $\kappa\tau_B \ll 1$. In energy space, this requires $\rho(\omega)$ as well as $n_F(\omega)$ to be approximately constant in the interval $\omega \in [\varepsilon_d - \kappa, \varepsilon_d + \kappa]$ which results in the condition

$$\kappa \ll \max\{k_B T, |\varepsilon_d - \mu|\}. \quad (163)$$

At low temperatures, the Fermi-Dirac distribution becomes a step function. Therefore, the Markovian approximation is not justified at low temperatures if the dot level ε_d is close to the chemical potential. For a more detailed discussion on the validity of the Born-Markov approximations, see appendix B.1 of Ref. [56].

IV.3.2. Solving the master equation

To solve the master equation in Eq. (160), we write the density matrix of the system as

$$\hat{\rho}_S(t) = p_0(t)|0\rangle\langle 0| + p_1(t)|1\rangle\langle 1|, \quad p_0(t) + p_1(t) = 1, \quad (164)$$

where $|0\rangle$ denotes the empty state and $|1\rangle$ the full state. Here we used the fact that we cannot have a superposition of states with a different number of electrons in the system due to a particle superselection rule [31]. Using these basis states, the fermionic operators can be cast into

$$\hat{d} = |0\rangle\langle 1|, \quad \hat{d}^\dagger = |1\rangle\langle 0|, \quad \hat{d}^\dagger \hat{d} = |1\rangle\langle 1|, \quad p_1(t) = \text{Tr}\{\hat{d}^\dagger \hat{d} \hat{\rho}_S(t)\}. \quad (165)$$

The master equation in Eq. (160) can then be reduced to

$$\partial_t p_1(t) = -\kappa[1 - n_F(\varepsilon_d)]p_1(t) + \kappa n_F(\varepsilon_d)p_0(t) = -\kappa[p_1(t) - n_F(\varepsilon_d)]. \quad (166)$$

This equation shows that a full dot is emptied with rate $\kappa[1 - n_F(\varepsilon_d)]$ whereas an empty dot is filled with rate $\kappa n_F(\varepsilon_d)$. The solution to this differential equation reads

$$p_1(t) = p_1(0)e^{-\kappa t} + n_F(\varepsilon_d)(1 - e^{-\kappa t}). \quad (167)$$

The occupation probability thus exponentially goes toward the equilibrium value $n_F(\varepsilon_d)$. The time-scale with which this happens is given by $1/\kappa$. In equilibrium, the system is described by the thermal state with temperature and chemical potential equal to those of the bath, as demanded by the zeroth law of thermodynamics, and we find

$$\lim_{t \rightarrow \infty} \hat{\rho}_S(t) = \frac{e^{-\beta(\varepsilon_d - \mu) \hat{d}^\dagger \hat{d}}}{\text{Tr}\{e^{-\beta(\varepsilon_d - \mu) \hat{d}^\dagger \hat{d}}\}}. \quad (168)$$

This result is closely related to the local detailed balance condition in Eq. (162).

IV.3.3. Energy flows and the first law

In addition to the state of the quantum dot, we are interested in the energy flow between the dot and the bath. To this end, we consider the change in the energy of the system

$$\partial_t \langle \hat{H}_S \rangle = \text{Tr}\{\varepsilon_d \hat{d}^\dagger \hat{d} \partial_t \hat{\rho}_S\} = (\varepsilon_d - \mu) \partial_t \langle \hat{d}^\dagger \hat{d} \rangle + \mu \partial_t \langle \hat{d}^\dagger \hat{d} \rangle = -J_B(t) - P_B(t). \quad (169)$$

To identify the heat current and the power, we used that the change in the number of electrons in the system is minus the change in the number of electrons in the bath. Using $p_1 = \langle \hat{d}^\dagger \hat{d} \rangle$, we find for the heat current and power that flow into the bath

$$\begin{aligned} J_B(t) &= -(\varepsilon_d - \mu) \partial_t \langle \hat{d}^\dagger \hat{d} \rangle = (\varepsilon_d - \mu) \kappa e^{-\kappa t} [p_1(0) - n_F(\varepsilon_d)], \\ P_B(t) &= -\mu \partial_t \langle \hat{d}^\dagger \hat{d} \rangle = \mu \kappa e^{-\kappa t} [p_1(0) - n_F(\varepsilon_d)]. \end{aligned} \quad (170)$$

We thus find that if the dot starts out in a non-equilibrium state, there is an exponentially decreasing energy flow which can be divided into power and heat. The power flows into the bath whenever $p_1(t) > n_F(\varepsilon_d)$. The heat flow additionally depends on the sign of $\varepsilon_d - \mu$: electrons entering the bath above the chemical potential ($\varepsilon_d - \mu > 0$) heat up the bath, while electrons entering below the chemical potential ($\varepsilon_d - \mu < 0$) cool it down. This can be understood intuitively by noting that at zero temperature, all states below the chemical potential are occupied while states above the chemical potential are empty. Electrons entering the bath below the chemical potential thus bring us closer to the zero-temperature distribution.

IV.3.4. Entropy and the second law

For the second law, we need to consider the entropy of the quantum dot given by

$$S_{vN}[\hat{\rho}_S(t)] = -p_0(t) \ln p_0(t) - p_1(t) \ln p_1(t), \quad \partial_t S_{vN}[\hat{\rho}_S(t)] = -\dot{p}_1(t) \ln \frac{p_1(t)}{1 - p_1(t)}, \quad (171)$$

where the dot denotes the time-derivative and we used $p_0 + p_1 = 1$ to compute the derivative. The entropy production rate given in Eq. (109) can then be expressed as

$$\dot{\Sigma}(t) = k_B \partial_t S_{vN}[\hat{\rho}_S(t)] + \frac{J_B}{T} = \frac{k_B J_B(t)}{(\varepsilon_d - \mu)} \left[\beta(\varepsilon_d - \mu) + \ln \frac{p_1(t)}{1 - p_1(t)} \right], \quad (172)$$

where we used $-\dot{p}_1 = J_B/(\varepsilon_d - \mu)$ which follows from Eq. (170). Using the equality

$$e^{\beta(\varepsilon_d - \mu)} = \frac{1 - n_F(\varepsilon_d)}{n_F(\varepsilon_d)}, \quad (173)$$

we find

$$\begin{aligned}\dot{\Sigma}(t) &= \frac{k_B J_B(t)}{(\varepsilon_d - \mu)} \ln \left(\frac{p_1(t)[1 - n_F(\varepsilon_d)]}{[1 - p_1(t)]n_F(\varepsilon_d)} \right) \\ &= k_B \kappa \left(p_1(t)[1 - n_F(\varepsilon_d)] - [1 - p_1(t)]n_F(\varepsilon_d) \right) \ln \left(\frac{p_1[1 - n_F(\varepsilon_d)]}{[1 - p_1]n_F(\varepsilon_d)} \right) \geq 0,\end{aligned}\tag{174}$$

where we used $J_B = (\varepsilon_d - \mu)\kappa(p_1 - n_F)$ which follows from Eqs. (166) and (170). the positivity of $\dot{\Sigma}$ can be shown by writing it in the form $(x - y)(\ln x - \ln y) \geq 0$ which is ensured to be positive because the logarithm is a monotonously increasing function. Using the solution in Eq. (167), we can explicitly write the entropy production rate as

$$\dot{\Sigma}(t) = k_B \kappa e^{-\kappa t} \delta_0 \ln \frac{(e^{-\kappa t} \delta_0 + n_F)(1 - n_F)}{(1 - n_F - e^{-\kappa t} \delta_0)n_F},\tag{175}$$

where we introduced $\delta_0 = p_1(0) - n_F$ and we suppressed the argument of the Fermi-Dirac distribution for ease of notation. We thus find that for this Markovian master equation, the entropy production rate is indeed always positive, as anticipated above, and exponentially decreases in time such that in equilibrium, no entropy is produced as expected.

IV.4. Obtaining GKLS form

We now return to Eq. (139). As mentioned above, this equation is not in GKLS form. In this section, we consider additional approximations that bring it into GKLS form. To this end, we first write

$$\tilde{S}_{\alpha,k}(t) = \sum_j e^{-i\omega_j t} \hat{S}_{\alpha,k}^j,\tag{176}$$

i.e., we write the system operators in Eq. (139) in a Fourier series. While this can always be done, it is particularly simple when the system Hamiltonian is time-independent. In this case, we may introduce its eigenstates as $\hat{H}_S |E_a\rangle = E_a |E_a\rangle$. We may then find the operators $\hat{S}_{\alpha,k}^j$ by multiplying $\hat{S}_{\alpha,k}$ from the left and the right by resolved identities

$$\hat{S}_{\alpha,k} = \sum_{a,b} \underbrace{|E_a\rangle\langle E_a| \hat{S}_{\alpha,k} |E_b\rangle\langle E_b|}_{\hat{S}_{\alpha,k}^j} \Rightarrow [\hat{S}_{\alpha,k}^j, \hat{H}_S] = \omega_j \hat{S}_{\alpha,k}^j,\tag{177}$$

with $\omega_j = E_b - E_a$.

With the help of Eq. (176), we may cast Eq. (139) into

$$\partial_t \tilde{\rho}_S(t) = \sum_{\alpha,k,k'} \sum_{j,j'} e^{i(\omega_j - \omega_{j'})t} \Gamma_{k,k'}^\alpha(\omega_{j'}) \left[\hat{S}_{\alpha,k'}^{j'} \tilde{\rho}_S(t) \left(\hat{S}_{\alpha,k}^j \right)^\dagger - \left(\hat{S}_{\alpha,k}^j \right)^\dagger \hat{S}_{\alpha,k'}^{j'} \tilde{\rho}_S(t) \right] + H.c.\tag{178}$$

with

$$\Gamma_{k,k'}^\alpha(\omega) \equiv \int_0^\infty ds e^{i\omega s} C_{k,k'}^\alpha(s) = \frac{1}{2} \gamma_{k,k'}^\alpha(\omega) + i \Delta_{k,k'}^\alpha(\omega),\tag{179}$$

where $\gamma_{k,k'}^\alpha(\omega)$ and $\Delta_{k,k'}^\alpha(\omega)$ are both real.

In the remainder of this section, we will consider a time-independent Hamiltonian \hat{H}_S , as well as bath-correlation functions that obey $C_{k,k'}^\alpha \propto \delta_{k,k'}$ for simplicity. This will simplify the notation as well as the derivation of the laws of thermodynamics for the master equations we consider.

IV.4.1. The secular approximation

The secular approximation is the most common approach for obtaining a master equation in GKLS form and can be found in many text-books (see for instance Ref. [45]). Let τ_S denote the time scale over which $\tilde{\rho}_S$ changes (remember that the Born-Markov approximations require $\tau_S \gg \tau_B$). The secular approximation is justified if

$$|\omega_j - \omega_{j'}| \tau_S \gg 1 \quad \forall j \neq j'. \quad (180)$$

In this case, we may drop all terms in Eq. (178) with $j \neq j'$ because they average out over a time-scale shorter than τ_S due to the oscillating term $\exp[i(\omega_j - \omega_{j'})t]$.

Going back to the Schrödinger picture, we then find the GKLS master equation

$$\partial_t \hat{\rho}_S(t) = -i[\hat{H}_S + \hat{H}_{LS}, \hat{\rho}_S(t)] + \sum_{\alpha, k, j} \gamma_k^\alpha(\omega_j) \mathcal{D}[\hat{S}_{\alpha, k}^j] \hat{\rho}_S(t), \quad (181)$$

where $\gamma_k^\alpha(\omega_j) = \gamma_{k, k}^\alpha(\omega_j)$ and the Lamb-shift Hamiltonian is given by

$$\hat{H}_{LS} = \sum_{\alpha, k, j} \Delta_k^\alpha(\omega_j) \left(\hat{S}_{\alpha, k}^j \right)^\dagger \hat{S}_{\alpha, k}^j, \quad (182)$$

with $\Delta_k^\alpha(\omega_j) = \Delta_{k, k}^\alpha(\omega_j)$. We note that from Eq. (177), it follows that $[\hat{H}_S, \hat{H}_{LS}] = 0$.

Due to Eq. (180), the secular approximation works well for systems which have no small gaps in \hat{H}_S . As we will see, thermal machines may consist of multiple parts that are weakly coupled and have small energy gaps induced by the weak coupling. In such systems, the secular approximation breaks down. Note that in order to obtain the jump operators $\hat{S}_{\alpha, k}^j$, the Hamiltonian \hat{H}_S needs to be diagonalized first. This implies that already obtaining the master equation may be a formidable task.

We note that in the secular approximation, for a non-degenerate system Hamiltonian, the populations decouple from the coherences. Indeed, the dissipative part of Eq. (181) describes classical jumps between the eigenstates of \hat{H}_S . Concretely, this means that in the energy-eigenbasis, the off-diagonal terms of the density matrix tend to zero and the dynamics can be described by a classical rate equation involving only the populations. While this may be a good approximation, there are many situations of interest where coherences between energy eigenstates are important in the presence of thermal baths and the secular approximation is no longer justified [57–62].

A particularly appealing feature of the secular approximation is the fact that the laws of thermodynamics are ensured to hold [10]:

0th law: If all baths are at the same inverse temperature β and chemical potential μ , then the steady state of Eq. (181) reduces to the Gibbs state

$$\hat{\rho}_S(t) \xrightarrow{t \rightarrow \infty} \frac{e^{\beta(\hat{H}_S - \mu \hat{N}_S)}}{\text{Tr} \left\{ e^{\beta(\hat{H}_S - \mu \hat{N}_S)} \right\}}. \quad (183)$$

In equilibrium, the system is thus described by the same temperature and chemical potential as the environment.

1st law: Writing the master equation in Eq. (181) as

$$\partial_t \hat{\rho}_S(t) = -i[\hat{H}_S + \hat{H}_{LS}, \hat{\rho}_S(t)] + \sum_{\alpha} \mathcal{L}_{\alpha} \hat{\rho}_S(t), \quad (184)$$

we find the first law as

$$\partial_t \langle \hat{H}_S \rangle = - \sum_{\alpha} [J_{\alpha}(t) + P_{\alpha}(t)], \quad (185)$$

with

$$J_{\alpha}(t) = -\text{Tr} \left\{ \left(\hat{H}_S - \mu_{\alpha} \hat{N}_S \right) \mathcal{L}_{\alpha} \hat{\rho}_S(t) \right\}, \quad P_{\alpha}(t) = -\mu_{\alpha} \text{Tr} \left\{ \hat{N}_S \mathcal{L}_{\alpha} \hat{\rho}_S(t) \right\}. \quad (186)$$

These definitions are to be compared with the definitions for the power and heat current in the general scenario, c.f. Eq. (105). There, we defined heat and work using the changes in the energy and particle numbers in the bath. When using a master equation for the reduced system state, we no longer have access to the properties of the bath. However, we may still infer heat and work because the term \mathcal{L}_{α} in the master equation describes the exchange of energy and particles with bath α . An increase in the particle number due to \mathcal{L}_{α} implies a decrease of the particle number in the bath by the same amount, and similarly for energy.

2nd law: The second law of thermodynamics also follows from Eq. (181) and it may be shown that [63, 64]

$$\dot{\Sigma} = k_B \partial_t S_{vN}[\hat{\rho}_S(t)] + \sum_{\alpha} \frac{J_{\alpha}(t)}{T_{\alpha}} \geq 0. \quad (187)$$

While we focused on a time-independent system Hamiltonian here, the secular approximation may analogously be applied for a time-dependent Hamiltonian and the laws of thermodynamics continue to hold in this case, see Ref. [10] and references therein.

IV.4.2. The singular-coupling limit

The singular-coupling limit [45, 47] is another popular approach to obtain a master equation in GKLS form. It is justified when all Bohr frequencies ω_j are close to each other, i.e.,

$$|\omega_j - \omega_{j'}| \tau_B \ll 1 \quad \forall j, j'. \quad (188)$$

In this case, we may write

$$\tilde{S}_{\alpha,k}(t-s) \sum_j e^{-i\omega_j(t-s)} \hat{S}_{\alpha,k}^j \simeq e^{i\omega_{\alpha,k}s} \sum_j e^{-i\omega_j t} \hat{S}_{\alpha,k}^j = e^{i\omega_{\alpha,k}s} \tilde{S}_{\alpha,k}(t), \quad (189)$$

where $\omega_{\alpha,k}$ has to be chosen such that $|\omega_{\alpha,k} - \omega_j| \tau_B \ll 1$ for all j . Because of Eq. (188), one may for instance choose $\omega_{\alpha,k}$ to equal the average of all ω_j . Equation (189) is justified for all $s \lesssim \tau_B$, i.e., exactly the values of s which are relevant in the integral of Eq. (139). As a consequence of Eq. (189), we may replace $\Gamma_k^{\alpha}(\omega_{j'})$ by $\Gamma_k^{\alpha}(\omega_{\alpha,k})$ in Eq. (178) which, in the Schrödinger picture, results in the GKLS master equation

$$\partial_t \hat{\rho}_S(t) = -i[\hat{H}_S + \hat{H}_{LS}, \hat{\rho}_S(t)] + \sum_{\alpha,k} \gamma_k^{\alpha}(\omega_{\alpha,k}) \mathcal{D}[\hat{S}_{\alpha,k}] \hat{\rho}_S(t), \quad (190)$$

where the Lamb-shift Hamiltonian reads

$$\hat{H}_{\text{LS}} = \sum_{\alpha,k} \Delta_k^\alpha(\omega_{\alpha,k}) \hat{S}_{\alpha,k}^\dagger \hat{S}_{\alpha,k}, \quad (191)$$

which does not necessarily commute with \hat{H}_S .

Note that the jump operators $\hat{S}_{\alpha,k}$ entering Eq. (190) are the operators that enter the coupling Hamiltonian \hat{V}_α . This implies that, in contrast to the secular approximation, the system Hamiltonian does not need to be diagonalized in order to write down the master equation. Since we are often interested in systems that are not explicitly solvable, this is very helpful.

We further note that the singular-coupling limit is always justified for a perfectly Markovian bath, i.e., a bath where $\tau_B \rightarrow 0$. More generally, the singular-coupling limit is justified when $\gamma_k^\alpha(\omega_j) \simeq \gamma_k^\alpha(\omega_{\alpha,k})$ for all j . This is often the case in quantum-optical systems, which is why the singular-coupling limit is widely applied in this community.

Showing that the laws of thermodynamics hold in the singular coupling limit is a bit more difficult than in the secular approximation. We first need to introduce a *thermodynamic Hamiltonian* \hat{H}_{TD} , which is obtained by rescaling the gaps of \hat{H}_S as $\omega_j \rightarrow \omega_{\alpha,k}$. The thermodynamic Hamiltonian is then used to compute the internal energy of the system. As argued in Ref. [56], the mistake we make by replacing \hat{H}_S with \hat{H}_{TD} in the thermodynamic bookkeeping is smaller than the resolution of heat that the master equation in Eq. (190) ensures. Within the accuracy of our model, the replacement is thus completely justified and in many cases it can be compared to neglecting the system-bath coupling in the thermodynamic bookkeeping. For the thermodynamic Hamiltonian, we find

$$[\hat{H}_{\text{TD}}, \hat{H}_S] = [\hat{H}_{\text{TD}}, \hat{H}_{\text{LS}}] = 0, \quad [\hat{S}_{\alpha,k}, \hat{H}_{\text{TD}}] = \omega_{\alpha,k} \hat{S}_{\alpha,k}. \quad (192)$$

The last equality implies that a jump $\hat{S}_{\alpha,k} \hat{\rho}_S \hat{S}_{\alpha,k}^\dagger$ reduces the internal energy by $\omega_{\alpha,k}$.

With the help of the thermodynamic Hamiltonian, the laws of thermodynamics may be shown to hold [56]:

0th law: If all baths are at the same inverse temperature β and chemical potential μ , then the steady state of Eq. (190) reduces to the Gibbs state

$$\hat{\rho}_S(t) \xrightarrow{t \rightarrow \infty} \frac{e^{\beta(\hat{H}_{\text{TD}} - \mu \hat{N}_S)}}{\text{Tr} \left\{ e^{\beta(\hat{H}_{\text{TD}} - \mu \hat{N}_S)} \right\}}. \quad (193)$$

In equilibrium, the system is thus described by the same temperature and chemical potential as the environment.

1st law: Writing the master equation in Eq. (190) as

$$\partial_t \hat{\rho}_S(t) = -i[\hat{H}_S + \hat{H}_{\text{LS}}, \hat{\rho}_S(t)] + \sum_{\alpha} \mathcal{L}_{\alpha} \hat{\rho}_S(t), \quad (194)$$

we find the first law as

$$\partial_t \langle \hat{H}_{\text{TD}} \rangle = - \sum_{\alpha} [J_{\alpha}(t) + P_{\alpha}(t)], \quad (195)$$

with

$$J_{\alpha}(t) = -\text{Tr} \left\{ \left(\hat{H}_{\text{TD}} - \mu_{\alpha} \hat{N}_S \right) \mathcal{L}_{\alpha} \hat{\rho}_S(t) \right\}, \quad P_{\alpha}(t) = -\mu_{\alpha} \text{Tr} \left\{ \hat{N}_S \mathcal{L}_{\alpha} \hat{\rho}_S(t) \right\}. \quad (196)$$

2nd law: The second law of thermodynamics also follows from Eq. (190) and it may be shown that

$$\dot{\Sigma} = k_B \partial_t S_{\text{vN}}[\hat{\rho}_S(t)] + \sum_{\alpha} \frac{J_{\alpha}(t)}{T_{\alpha}} \geq 0. \quad (197)$$

As for the secular approximation, the results from this section may be extended to a time-dependent Hamiltonian and the laws of thermodynamics continue to hold in this case [56].

We note that in particular in thermodynamic contexts, it is often the case that there are positive and negative Bohr frequencies, with each $\tilde{S}_{\alpha,k}(t)$ containing only involves frequencies of one sign. In this case, we may perform the singular coupling limit for the positive and negative Bohr frequencies separately. In this case, the master equation in Eq. (190) is also valid if Eq. (188) is only respected for frequencies ω_j and $\omega_{j'}$ of the same sign. Below, we will discuss an example where this is the case.

IV.4.3. The unified GKLS master equation

Finally, we briefly mention an approach to obtain GKLS form for systems where neither the secular approximation nor the singular-coupling limit is justified [56, 65]. The problem is that for some values of j and j' , we may find $|\omega_j - \omega_{j'}| \tau_S \lesssim 1$, rendering the secular approximation inapplicable, while for other values of j and j' , we may have $|\omega_j - \omega_{j'}| \tau_B \gtrsim 1$, such that the singular-coupling limit may not be applied. The solution for this problem exploits the fact that $\tau_B \ll \tau_S$, otherwise the Born-Markov approximations are not justified in the first place. This inequality implies that for all values of j and j' , we either have $|\omega_j - \omega_{j'}| \tau_S \gg 1$ or we have $|\omega_j - \omega_{j'}| \tau_B \ll 1$. One may then perform the following approximations to reach GKLS form:

1. Drop all terms with j and j' such that $|\omega_j - \omega_{j'}| \tau_S \gg 1$, in analogy to the secular approximation.
2. Perform a singular-coupling limit on the remaining cross terms with $\omega_j \neq \omega_{j'}$.

The resulting master equation also obeys the laws of thermodynamics for an appropriately chosen thermodynamic Hamiltonian.

IV.5. Example: A double quantum dot

We now consider an example provided by a double quantum dot, coupled to two fermionic reservoirs. We again consider spinless electrons, such that each dot can at maximum host one electron. Furthermore, we consider two dots in series, such that each dot is coupled to one of the reservoirs. The total Hamiltonian that describes this scenario is given by

$$\hat{H}_{\text{tot}} = \hat{H}_S + \hat{H}_L + \hat{H}_R + \hat{V}_L + \hat{V}_R, \quad (198)$$

with the system Hamiltonian

$$\hat{H}_S = \varepsilon \hat{d}_L^\dagger \hat{d}_L + \varepsilon \hat{d}_R^\dagger \hat{d}_R + g(\hat{d}_L^\dagger \hat{d}_R + \hat{d}_R^\dagger \hat{d}_L) = (\varepsilon + g) \hat{d}_+^\dagger \hat{d}_+ + (\varepsilon - g) \hat{d}_-^\dagger \hat{d}_-, \quad (199)$$

where we chose the on-site energies ε of the two dots to be equal for simplicity and we introduced the eigenmodes

$$\hat{d}_{\pm} = \frac{1}{\sqrt{2}} (\hat{d}_R \pm \hat{d}_L), \quad \hat{d}_R = \frac{1}{\sqrt{2}} (\hat{d}_+ + \hat{d}_-), \quad \hat{d}_L = \frac{1}{\sqrt{2}} (\hat{d}_+ - \hat{d}_-). \quad (200)$$

The reservoirs are again modeled by a collection of non-interacting electrons that are tunnel-coupled to the respective dots

$$\hat{H}_\alpha = \sum_q \varepsilon_{\alpha,q} \hat{c}_{\alpha,q}^\dagger \hat{c}_{\alpha,q}, \quad \hat{V}_\alpha = \sum_q \left(g_{\alpha,q} \hat{d}_\alpha \hat{c}_{\alpha,q}^\dagger - g_{\alpha,q}^* \hat{d}_\alpha^\dagger \hat{c}_{\alpha,q} \right), \quad (201)$$

with $\alpha = \text{L, R}$. As in the example of a single quantum dot, we may write the coupling Hamiltonian as $\hat{V}_\alpha = \hat{S}_{\alpha,0} \hat{B}_{\alpha,0} + \hat{S}_{\alpha,1} \hat{B}_{\alpha,1}$ and we find

$$\begin{aligned} \tilde{S}_{\text{R},0}(t) &= e^{i\hat{H}_\text{S}t} \hat{d}_\text{R} e^{-i\hat{H}_\text{S}t} = e^{-i(\varepsilon+g)t} \frac{\hat{d}_+}{\sqrt{2}} + e^{-i(\varepsilon-g)t} \frac{\hat{d}_-}{\sqrt{2}}, \\ \tilde{S}_{\text{L},0}(t) &= e^{i\hat{H}_\text{S}t} \hat{d}_\text{L} e^{-i\hat{H}_\text{S}t} = e^{-i(\varepsilon+g)t} \frac{\hat{d}_+}{\sqrt{2}} - e^{-i(\varepsilon-g)t} \frac{\hat{d}_-}{\sqrt{2}}. \end{aligned} \quad (202)$$

Comparing these expressions to Eq. (176), we may read off the frequencies $\omega_j = \varepsilon \pm g$, as well as the corresponding operators $\hat{S}_{\alpha,0}^j$. Similarly, we find $\tilde{S}_{\alpha,1}(t) = \tilde{S}_{\alpha,0}^\dagger(t)$, which involve the frequencies $\omega_j = -(\varepsilon \pm g)$.

The bath correlation functions are obtained in analogy to the single-dot case in Sec. IV.3 and read

$$C_{0,0}^\alpha(s) = \int_{-\infty}^{\infty} d\omega e^{-i\omega s} \rho_\alpha(\omega) [1 - n_\text{F}^\alpha(\omega)], \quad C_{1,1}^\alpha(s) = \int_{-\infty}^{\infty} d\omega e^{i\omega s} \rho_\alpha(\omega) n_\text{F}^\alpha(\omega), \quad (203)$$

with the Fermi-Dirac distribution

$$n_\text{F}^\alpha(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu_\alpha}{k_B T_\alpha}} + 1}. \quad (204)$$

Furthermore, from Eq. (179) we find the relevant transition rates

$$\gamma_0^\alpha(\omega) = \kappa_\alpha [1 - n_\text{F}^\alpha(\omega)], \quad \gamma_1^\alpha(-\omega) = \kappa_\alpha n_\text{F}^\alpha(\omega), \quad (205)$$

where $\kappa_\alpha = 2\pi\rho_\alpha(\omega)$, as well as the energy shifts

$$\Delta_0^\alpha(\omega) = P \int_{-\infty}^{\infty} d\omega' \frac{\rho_\alpha(\omega') [1 - n_\text{F}^\alpha(\omega')]}{\omega - \omega'}, \quad \Delta_1^\alpha(-\omega) = -P \int_{-\infty}^{\infty} d\omega' \frac{\rho_\alpha(\omega') n_\text{F}^\alpha(\omega')}{\omega - \omega'}. \quad (206)$$

Note the different signs in the arguments of the functions with different subscripts. As we will see below, these functions will be evaluated at frequencies of opposite signs. From the bath correlation functions, we conclude that the Born-Markov approximations are justified when

$$\rho_\alpha(\varepsilon \pm g \pm \kappa) \simeq \rho_\alpha(\varepsilon \pm g), \quad n_\text{F}^\alpha(\varepsilon \pm g \pm \kappa) \simeq n_\text{F}^\alpha(\varepsilon \pm g), \quad (207)$$

where $\kappa = \max\{\kappa_\text{L}, \kappa_\text{R}\}$.

IV.5.1. The secular approximation

Identifying all the quantities appearing in Eq. (181), we find the GKLS master equation in the secular approximation

$$\begin{aligned} \partial_t \hat{\rho}_\text{S}(t) &= -i \left[\sum_{\sigma=\pm} \bar{\varepsilon}_\sigma \hat{d}_\sigma^\dagger \hat{d}_\sigma, \hat{\rho}_\text{S}(t) \right] \\ &+ \sum_{\alpha=\text{L,R}} \sum_{\sigma=\pm} \frac{\kappa_\alpha}{2} \left\{ n_\text{F}^\alpha(\varepsilon_\sigma) \mathcal{D}[\hat{d}_\sigma^\dagger] + [1 - n_\text{F}^\alpha(\varepsilon_\sigma)] \mathcal{D}[\hat{d}_\sigma] \right\} \hat{\rho}_\text{S}(t), \end{aligned} \quad (208)$$

with the energies

$$\varepsilon_{\pm} = \varepsilon \pm g, \quad \bar{\varepsilon}_{\pm} = \varepsilon_{\pm} + P \int_{-\infty}^{\infty} d\omega \frac{\rho_L(\omega) + \rho_R(\omega)}{\varepsilon \pm g - \omega}. \quad (209)$$

The master equation in the secular approximation describes classical hopping into and out of the delocalized eigenmodes described by the operators \hat{d}_{\pm} . Any coherences between these eigenmodes decay. We may thus interpret the secular master equation as a classical master equation. However, note that the eigenmodes themselves describe electrons being in a coherent superposition between the two dots.

Evaluating Eq. (186), we find the heat flow and power

$$J_{\alpha} = \sum_{\sigma=\pm} \frac{\varepsilon_{\sigma} - \mu_{\alpha}}{2} \kappa_{\alpha} \left[\langle \hat{d}_{\sigma}^{\dagger} \hat{d}_{\sigma} \rangle - n_F^{\alpha}(\varepsilon_{\sigma}) \right], \quad P_{\alpha} = \mu_{\alpha} \sum_{\sigma=\pm} \frac{\kappa_{\alpha}}{2} \left[\langle \hat{d}_{\sigma}^{\dagger} \hat{d}_{\sigma} \rangle - n_F^{\alpha}(\varepsilon_{\sigma}) \right]. \quad (210)$$

From Eq. (180), we conclude that the secular approximation is justified when

$$\frac{1}{\tau_S} = \kappa_{\alpha} \ll g = \frac{1}{2} |\omega_j - \omega_{j'}|. \quad (211)$$

This implies that for strong coupling between the dots, the secular approximation can safely be applied. However, once the coupling g becomes comparable to κ , it is no longer justified. In this case, one should apply the singular-coupling limit.

IV.5.2. The singular-coupling limit

In the singular-coupling limit, we make the replacement

$$\tilde{S}_{\alpha,0}(t-s) \simeq e^{i\varepsilon s} \tilde{S}_{\alpha,0}(t), \quad \tilde{S}_{\alpha,1}(t-s) \simeq e^{-i\varepsilon s} \tilde{S}_{\alpha,1}(t). \quad (212)$$

This implies that the frequencies appearing in Eq. (190) are $\omega_{\alpha,0} = \varepsilon$ and $\omega_{\alpha,1} = -\varepsilon$. We note that there is no restriction on $|\omega_{\alpha,0} - \omega_{\alpha,1}|$ because $\tilde{S}_{\alpha,0}$ only involves the frequencies $\varepsilon \pm g$ while $\tilde{S}_{\alpha,1}$ only involves the frequencies $-(\varepsilon \pm g)$. With the substitution in Eq. (212), we find the GKLS master equation

$$\partial_t \hat{\rho}_S(t) = -i[\hat{H}_S + \hat{H}_{LS}, \hat{\rho}_S(t)] + \sum_{\alpha=L,R} \kappa_{\alpha} \left\{ n_F^{\alpha}(\varepsilon) \mathcal{D}[\hat{d}_{\alpha}^{\dagger}] + [1 - n_F^{\alpha}(\varepsilon)] \mathcal{D}[\hat{d}_{\alpha}] \right\} \hat{\rho}_S(t), \quad (213)$$

with the Lamb-shift Hamiltonian

$$\hat{H}_{LS} = \Delta_L \hat{d}_L^{\dagger} \hat{d}_L + \Delta_R \hat{d}_R^{\dagger} \hat{d}_R, \quad \Delta_{\alpha} = P \int_{-\infty}^{\infty} d\omega \frac{\rho_{\alpha}(\omega)}{\varepsilon - \omega}. \quad (214)$$

The master equation in the singular coupling limit is also known as a *local* master equation, because the jump operators act locally on the left and right quantum dots. In contrast to the secular master equation (also denoted *global* master equation), the populations and coherences do not decouple and we may find coherence and even entanglement between the two quantum dots [62]. We note that the local master equation may also be obtained heuristically by first setting $g = 0$, deriving the master equation as in Sec. IV.3, and then reinstating g in the Hamiltonian. For certain scenarios, this heuristic approach may result in master equations that violate the laws of thermodynamics [66]. For this reason, it is recommended to perform

the singular-coupling approximation as outlined above. We then obtain a thermodynamically consistent framework with the thermodynamic Hamiltonian

$$\hat{H}_{\text{TD}} = \varepsilon \left(\hat{d}_{\text{L}}^\dagger \hat{d}_{\text{L}} + \hat{d}_{\text{R}}^\dagger \hat{d}_{\text{R}} \right). \quad (215)$$

In the thermodynamic bookkeeping, we thus neglect the coupling between the dots, in analogy to how we neglect the system-bath coupling energy.

Evaluating Eq. (196), we find the heat flow and power

$$J_\alpha = \kappa_\alpha (\varepsilon - \mu_\alpha) \left[\langle \hat{d}_\alpha^\dagger \hat{d}_\alpha \rangle - n_{\text{F}}^\alpha(\varepsilon) \right], \quad P_\alpha = \kappa_\alpha \mu_\alpha \left[\langle \hat{d}_\alpha^\dagger \hat{d}_\alpha \rangle - n_{\text{F}}^\alpha(\varepsilon) \right]. \quad (216)$$

In this approximation, each electron that enters bath α carries the heat $\varepsilon - \mu_\alpha$ and the power μ_α , resulting in the simple relation $J_\alpha/P_\alpha = (\varepsilon - \mu_\alpha)/\mu_\alpha$.

The singular coupling limit is justified when $\rho_\alpha(\varepsilon \pm g) \simeq \rho_\alpha(\varepsilon)$ as well as $n_{\text{F}}^\alpha(\varepsilon \pm g) \simeq n_{\text{F}}^\alpha(\varepsilon)$. The second condition is obeyed when

$$g \ll \max\{k_{\text{B}}T_\alpha, |\varepsilon - \mu_\alpha|\}. \quad (217)$$

Note that $g \ll \kappa$ is *not* required for the singular-coupling limit to be justified. The secular approximation and the singular-coupling limit may thus be justified at the same time. Indeed, since $\tau_{\text{S}} \gg \tau_{\text{B}}$ this is what we expect from Eqs. (180) and (188).

V. Quantum thermal machines

In this section, we consider quantum thermal machines, i.e., machines that use reservoirs in local equilibrium to perform a useful task such as converting heat into work or producing entanglement. While in local equilibrium, these reservoirs have different temperatures and/or chemical potentials such that together, they describe an out-of-equilibrium scenario.

V.1. Heat engine

The first machine we consider is a simplified version of the heat engine that was implemented experimentally in Ref. [67]. In contrast to a quantum dot coupled to a single bath, where the only thing that happens is thermalization, we will find heat flows in the steady state and we will see how heat can be converted into work and how work can be used to refrigerate. The system we consider is a spinless, single-level quantum dot tunnel-coupled to two heat baths

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{S}} + \hat{H}_{\text{c}} + \hat{H}_{\text{h}} + \hat{V}_{\text{c}} + \hat{V}_{\text{h}}, \quad (218)$$

with

$$\hat{H}_{\text{S}} = \varepsilon_{\text{d}} \hat{d}^\dagger \hat{d}, \quad \hat{H}_\alpha = \sum_q \varepsilon_{\alpha,q} \hat{c}_{\alpha,q}^\dagger \hat{c}_{\alpha,q}, \quad \hat{V}_\alpha = \hat{d} \sum_q g_{\alpha,q} \hat{c}_{\alpha,q}^\dagger - \hat{d}^\dagger \sum_q g_{\alpha,q}^* \hat{c}_{\alpha,q}, \quad (219)$$

where $\alpha = \text{c, h}$ labels the baths according to their temperatures $T_{\text{c}} \leq T_{\text{h}}$. Just as for the quantum dot coupled to a single bath, Eq. (139) is already in GKLS form. Since the terms in the master equation corresponding to different baths are additive, we find

$$\partial_t \hat{\rho}_{\text{S}} = -i[\hat{H}_{\text{S}}, \hat{\rho}_{\text{S}}] + \mathcal{L}_{\text{c}} \hat{\rho}_{\text{S}} + \mathcal{L}_{\text{h}} \hat{\rho}_{\text{S}}, \quad (220)$$

with

$$\mathcal{L}_\alpha \hat{\rho} = \kappa_\alpha [1 - n_F^\alpha(\varepsilon_d)] \mathcal{D}[\hat{d}^\dagger] \hat{\rho} + \kappa_\alpha n_F^\alpha(\varepsilon_d) \mathcal{D}[\hat{d}] \hat{\rho}, \quad (221)$$

where n_F^α is the Fermi-Dirac distribution with temperature T_α and chemical potential μ_α , see Eq. (204). Here we neglected the renormalization of ε_d which is given by a straightforward generalization of Eq. (161).

V.1.1. Solving the master equation

The master equation can easily be solved by considering

$$\partial_t p_1 = \text{Tr}\{\hat{d}^\dagger \hat{d} \partial_t \hat{\rho}_S\} = - \sum_{\alpha=c,h} \kappa_\alpha \{[1 - n_F^\alpha(\varepsilon_d)] p_1 - n_F^\alpha(\varepsilon_d) p_0\} = -\gamma(p_1 - \bar{n}), \quad (222)$$

where

$$\gamma = \kappa_c + \kappa_h, \quad \bar{n} = \frac{\kappa_c n_F^c(\varepsilon_d) + \kappa_h n_F^h(\varepsilon_d)}{\kappa_c + \kappa_h}. \quad (223)$$

Comparing to Eq. (166), we find that the quantum dot behaves just like a quantum dot coupled to a single heat bath with coupling strength γ and mean occupation \bar{n} . The solution thus reads

$$p_1(t) = p_1(0) e^{-\gamma t} + \bar{n}(1 - e^{-\gamma t}). \quad (224)$$

V.1.2. The first law

From the master equation, we find the first law

$$\partial_t \langle \hat{H}_S \rangle = \varepsilon_d \text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_c \hat{\rho}_S\} + \varepsilon_d \text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_h \hat{\rho}_S\} = -J_c - P_c - J_h - P_h, \quad (225)$$

where the power and heat currents are defined in agreement with Eq. (186)

$$P_\alpha = -\mu_\alpha \text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_\alpha \hat{\rho}_S\}, \quad J_\alpha = -(\varepsilon_d - \mu_\alpha) \text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_\alpha \hat{\rho}_S\}. \quad (226)$$

Explicitly, we find

$$P_\alpha = \mu_\alpha \kappa_\alpha e^{-\gamma t} [p_1(0) - \bar{n}] + \mu_\alpha \kappa_\alpha [\bar{n} - n_F^\alpha(\varepsilon_d)], \quad J_\alpha = \frac{\varepsilon_d - \mu_\alpha}{\mu_\alpha}. \quad (227)$$

Just as for a single bath, there is a transient term in the power which decreases exponentially in time. In contrast to the single bath case, there is now also a time-independent term which remains in steady state.

In the steady state, the observables of the system do not change. We can use this fact to draw a number of conclusions without using the explicit solutions for the power and the heat currents. In particular, since the left-hand side of Eq. (225) vanishes, we find

$$\text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_c \hat{\rho}_S\} = -\text{Tr}\{\hat{d}^\dagger \hat{d} \mathcal{L}_h \hat{\rho}_S\}. \quad (228)$$

From this, using Eqs. (226), follows

$$P = P_c + P_h = -(J_c + J_h), \quad (229)$$

which is nothing but the first law, as well as

$$\eta = \frac{P}{-J_h} = \frac{\mu_c - \mu_h}{\varepsilon_d - \mu_h} = 1 - \frac{\varepsilon_d - \mu_c}{\varepsilon_d - \mu_h}, \quad (230)$$

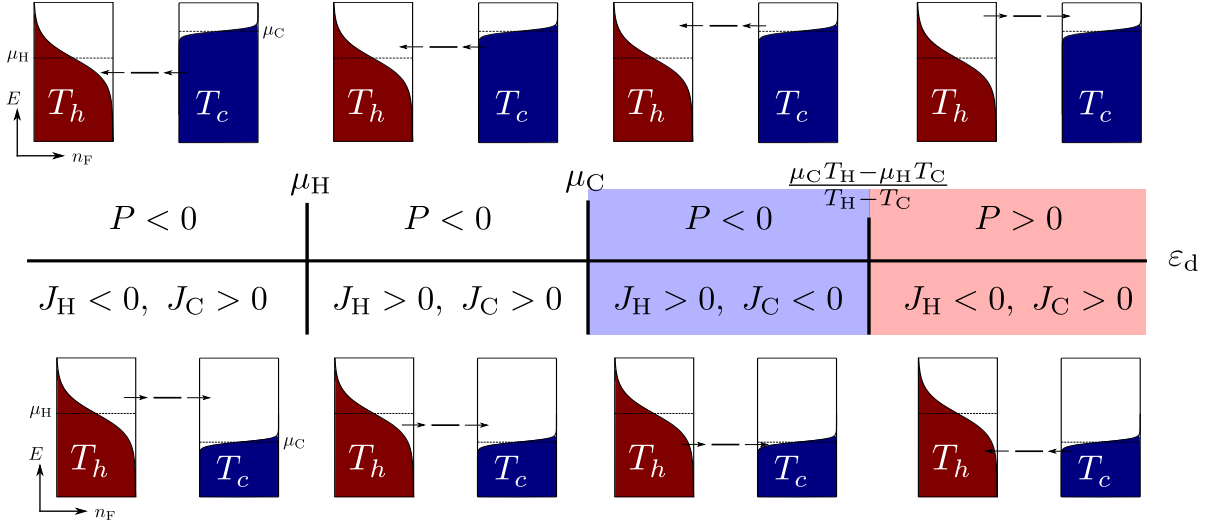


Figure 9: Different regimes determined by the signs of P , J_c , and J_h . For $\mu_c \geq \mu_h$, ε_d increases from left to right (illustrated by the cartoons in the upper row). For $\mu_c \leq \mu_h$, we find the exact same regimes but ε_d decreases from left to right (illustrated by the cartoons in the lower row). In the regime to the far left, heat flows out of the hot bath and into the cold bath and power is dissipated. If ε_d lies in between the chemical potentials, both baths are heated up by the dissipated power. Refrigeration is obtained in the blue shaded regime, where heat is extracted from the cold bath and dumped into the hot bath. Finally, in the red shaded regime the quantum dot acts as a heat engine where a heat flow from hot to cold drives a charge flow against the external voltage bias.

where we introduced the efficiency η which is given by the ratio between the power (the output of the heat engine) and the heat current from the hot bath (the input of the heat engine). Using the explicit solution for the power in Eq. (227), we find

$$P = \frac{\kappa_c \kappa_h}{\kappa_c + \kappa_h} (\mu_c - \mu_h) [n_F^h(\varepsilon_d) - n_F^c(\varepsilon_d)]. \quad (231)$$

This quantity vanishes at zero voltage ($\mu_c = \mu_h$), as well as at the stopping voltage where $n_F^h(\varepsilon_d) = n_F^c(\varepsilon_d)$, see also Fig. 10 b).

Let us now consider under which conditions the system acts as a heat engine, i.e., heat from the hot bath is converted into power. From Eq. (231), we can identify different regimes depending on the signs of P , J_c , and J_h . These regimes are illustrate in Figs. 9 and 10 (a). For $\mu_c \geq \mu_h$ ($\mu_c \leq \mu_h$), we find that the quantum dot acts as a heat engine for large positive (negative) values of ε_d . In both cases, we find from Eq. (231) that power is positive as long as

$$\frac{\varepsilon_d - \mu_c}{\varepsilon_d - \mu_h} \geq \frac{T_c}{T_h} \quad \Rightarrow \quad \eta \leq 1 - \frac{T_c}{T_h} = \eta_C. \quad (232)$$

We thus find that the efficiency is bounded from above by the Carnot efficiency as long as the power output is non-negative.

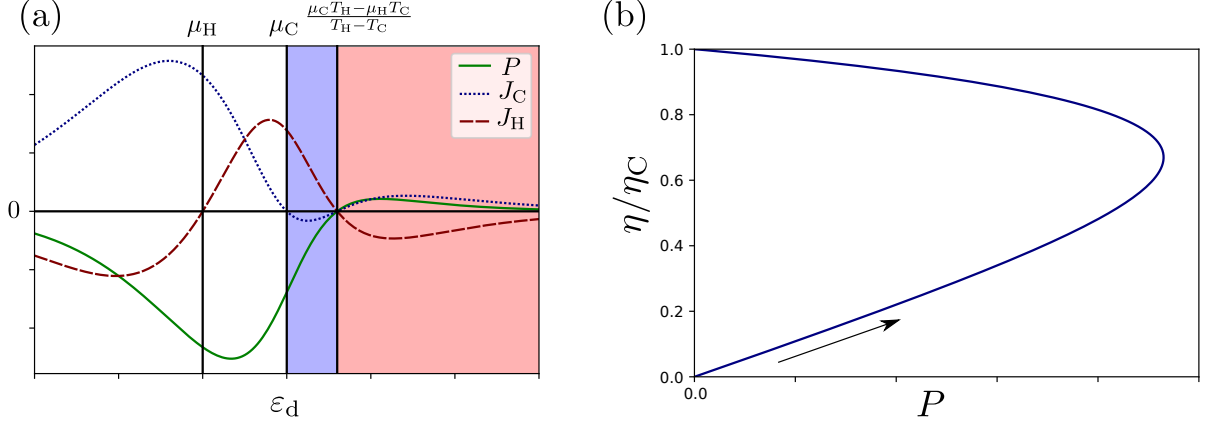


Figure 10: Performance of the quantum dot heat engine. (a) Power and heat currents as a function of ε_d . The regimes illustrated in Fig. 9 can clearly be identified. (b) “Lasso” diagram. Along the curve, the voltage bias is increased in the direction of the arrow. For $\mu_c = \mu_h$, both the power as well as the efficiency vanishes. Increasing μ_c then results in a finite power and efficiency, until the power vanishes again at the stopping voltage, where the efficiency reaches η_C . Such plots are called Lasso diagrams because the curve usually goes back to the origin at the stopping voltage. Parameters: $\kappa_c = \kappa_h$, $\varepsilon_d = 2\kappa_c$, $T_c = 0.3\kappa_c$, $T_h = 0.8\kappa_c$, $\mu_c = \kappa_c$, $\mu_h = 0$, .

V.1.3. The second law

We first make some general statements about the second law in a two-terminal setup. These are very similar to the statements made in Sec. I.2. The entropy production rate is given by

$$\dot{\Sigma} = \partial_t S_{\text{vN}}[\hat{\rho}_S] + \frac{J_c}{k_B T_c} + \frac{J_h}{k_B T_h} \geq 0. \quad (233)$$

In the steady state, the first term vanishes and we immediately find that at least one of the heat currents has to be positive. This implies that it is impossible to cool down all baths at the same time (in the steady state). Furthermore, for equal temperatures ($T_c = T_h$), we find $P = -(J_c + J_h) \leq 0$ which implies that it is not possible to convert heat into work with baths at a single temperature. This is known as the Kelvin-Planck statement of the second law. Finally, we can use the first law in Eq. (229) to eliminate J_c , resulting in

$$\dot{\Sigma} = \frac{P}{k_B T_c} \frac{\eta_C - \eta}{\eta} \Rightarrow 0 \leq \eta \leq \eta_C, \quad (234)$$

where the last inequality holds for $P \geq 0$. The fact that the efficiency is upper bounded by the Carnot efficiency is thus a direct consequence of the second law.

In our system, the entropy of the quantum dot is given in Eq. (171). Using

$$\partial_t p_1 = -\frac{J_c}{\varepsilon_d - \mu_c} - \frac{J_h}{\varepsilon_d - \mu_h}, \quad (235)$$

we can write the entropy production rate as

$$\dot{\Sigma} = \sum_{\alpha=c,h} \kappa_\alpha \left(p_1 [1 - n_F^\alpha(\varepsilon_d)] - [1 - p_1] n_F^\alpha(\varepsilon_d) \right) \ln \left(\frac{p_1 [1 - n_F^\alpha(\varepsilon_d)]}{[1 - p_1] n_F^\alpha(\varepsilon_d)} \right) \geq 0, \quad (236)$$

which is positive since each term in the sum is positive in complete analogy to Eq. (174). In the steady state, we find

$$\dot{\Sigma} = \frac{\kappa_c \kappa_h}{\kappa_c + \kappa_h} [n_F^h(\varepsilon_d) - n_F^c(\varepsilon_d)] [\beta_c(\varepsilon_d - \mu_c) - \beta_h(\varepsilon_d - \mu_h)] \geq 0, \quad (237)$$

which vanishes at the Carnot point, where $n_F^h(\varepsilon_d) = n_F^c(\varepsilon_d)$, $\eta = \eta_C$, and both the power as well as the heat currents vanish. We stress that while an equilibrium situation (i.e., $T_c = T_h$ and $\mu_c = \mu_h$) ensures $n_F^h(\varepsilon_d) = n_F^c(\varepsilon_d)$, the Carnot point can also be reached out of equilibrium.

The interplay between power and efficiency is illustrated in Fig. 10. We find that at maximum power, the efficiency reaches above 60% of the Carnot efficiency. Similar values were found experimentally in Ref. [67]. As mentioned above, the Carnot efficiency is obtained at the stopping voltage. This is a consequence of the fact that there is only a single energy at which transport happens. At the stopping voltage, all transport is blocked implying that both the charge as well as the heat currents vanish. This implies that there is no dissipation ($\dot{\Sigma} = 0$) and the efficiency takes on the Carnot value (see also Ref. [68]). In reality, as well as in the experiment of Ref. [67], this ideal filtering effect is spoiled by the broadening of the energy level which is neglected in the Markovian master equation. Including this energy broadening, one finds that at some energies, charges move from hot to cold while at other energies, they move in the other direction. At the stopping voltage, this results in a vanishing of power but still a net heat current, such that the efficiency vanishes. In this case, Fig. 10 (b) takes on the shape of a lasso.

V.1.4. Refrigeration

As discussed above, the quantum dot can also act as a refrigerator in the regime where $P < 0$, $J_h > 0$, and $J_c < 0$. In this case, electrical power is used to reverse the natural flow of heat, resulting in a heat flow out of the cold bath and into the hot bath. The efficiency of this process is usually characterized by the coefficient of performance (COP)

$$\eta^{\text{COP}} = \frac{-J_c}{-P}, \quad (238)$$

where we left the minus signs to stress that this performance quantifier is relevant in the regime where both P as well as J_c are negative under our sign convention. We can use the first law in Eq. (229) to eliminate J_h and write the entropy production rate as

$$\dot{\Sigma} = \frac{-J_c}{k_B T_h} \frac{\eta_C^{\text{COP}} - \eta^{\text{COP}}}{\eta_C^{\text{COP}} \eta^{\text{COP}}} \Rightarrow 0 \leq \eta^{\text{COP}} \leq \eta_C^{\text{COP}}, \quad (239)$$

where the second inequality holds for $J_c \leq 0$ and we introduced the Carnot value for the COP

$$\eta_C^{\text{COP}} = \frac{T_c}{T_h - T_c}. \quad (240)$$

We note that as $T_c \rightarrow T_h$, η_C^{COP} diverges. This reflects the fact that in principle, it is possible to move heat in between two baths with equal temperature without investing any work.

In our system, we find from Eqs. (226) and (228)

$$\eta^{\text{COP}} = \frac{\mu_c - \varepsilon_d}{\mu_c - \mu_h}. \quad (241)$$

From this, we find that η^{COP} vanishes when $\varepsilon_d = \mu_c$ and takes on the Carnot value at $\varepsilon_d = \frac{\mu_c T_h - \mu_h T_c}{T_h - T_c}$, which is exactly the point where the regime of the refrigerator meets the regime of the heat engine, see Fig. 9. Interestingly, both the COP as well as the efficiency reach their maximum value at this point, where no transport takes place. The Carnot point is often called the point of *reversibility*. At this point nothing happens but it can be seen as the limit of converting heat into work infinitely slowly and without wasting any energy (thus, reversibly). Equivalently, taking the limit from the other side, it can be seen as the limit of cooling the cold bath reversibly.

V.2. Entanglement generator

V.3. Absorption refrigerator

VI. Fluctuations

VII. Summary

VIII. Outlook

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