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A study of the thermodynamic principles and implementations of the quantum Otto engine

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Monography in Physics

Rafael do Lago Souza Costa

Goiânia, 2023
Brazil

UNIVERSIDADE FEDERAL DE GOIÁS
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Rafael do Lago Souza Costa

A study of the thermodynamic principles and implementations of the quantum Otto engine

Monography presented to the Institute of Physics of the Federal University of Goiás as partial requirement to obtain the Bachelor's degree in Physics.

ADVISOR: Prof. Dr. Lucas Chibebe Céleri

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ATA DE DEFESA DE TRABALHO DE CONCLUSÃO DE CURSO

Aos 11 dias do mês de Agosto de 2023, a partir das 10h30min realizou-se a sessão pública de Defesa de Trabalho de Conclusão de Curso do estudante do curso de Física, Bacharelado, **Rafael do Lago Souza Costa,** matrícula 202108047, para apresentar sua monografia intitulada: "**A study of the thermodynamic principles and implementations of the quantum Otto engine**". A banca examinadora foi composta pelos professores **Lucas Chibebe Céleri** (IF/UFG), **Renato Borges Pontes** (IF/UFG) e **Vanuildo Silva de Carvalho** (IF/UFG). A sessão pública de Defesa de TCC foi aberta pelo Presidente da Banca Examinadora, Professor Lucas Chibebe Céleri (Orientador), que na sequência passou a palavra para o estudante apresentar sua monografia. Após a exposição, a Banca Examinadora realizou a arguição do estudante. Ao finalizar a arguição, a Banca reuniu-se em sessão secreta a fim de concluir o julgamento da monografia. A Banca atribuiu ao estudante a nota **9,00**, este foi **APROVADO** na disciplina de TCC. Proclamados os resultados pelo Professor Lucas Chibebe Céleri (Presidente), foram encerrados os trabalhos e, para constar, lavrou-se a presente ata que é assinada pelos membros da Banca Examinadora.

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“The only true wisdom is knowing you know nothing.”

Socrates

“To my younger brother, José Pedro.”

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Abstract

This monography provides a comprehensive overview of classical and quantum thermodynamics. The classical formulations of thermodynamics are discussed in detail, including concepts such as energy and equilibrium, ideal gases and internal energy. Study the first and second laws of thermodynamics and their applications to mechanical work, heat engines and thermodynamic cycles. The present work also covers some quantum thermodynamics principles, including the use of density operators to describe pure and mixed states of quantum systems and the time evolution of these operators. The first law of quantum thermodynamics is introduced, along with the concepts of quantum adiabatic evolution and quantum Otto cycles. In addition, this monography briefly discusses the concept of Maxwell's demon in the context of quantum thermodynamics and its implications for the second law. Overall, this work provides a comprehensive introduction to the basic principles of classical and quantum thermodynamics.

Keywords: Thermodynamics; quantum heat engines; o tto cycle.

Resumo

Esta monografia oferece uma visão abrangente da termodinâmica clássica e quântica. As formulações clássicas da termodinâmica são discutidas em detalhes, incluindo conceitos como energia e equilíbrio, gases ideais e energia interna. São estudadas a primeira e a segunda lei da termodinâmica, bem como suas aplicações em trabalho mecânico, motores térmicos e ciclos termodinâmicos. Este trabalho também aborda alguns princípios da termodinâmica quântica, incluindo o uso de operadores de densidade para descrever estados puros e mistos de sistemas quânticos e a evolução temporal desses operadores. A primeira lei da termodinâmica quântica é introduzida, juntamente com os conceitos de evolução adiabática quântica e o ciclo de Otto quântico. Além disso, esta monografia discute brevemente o conceito do demônio de Maxwell no contexto da termodinâmica quântica e suas implicações para a segunda lei. No geral, este trabalho oferece uma introdução abrangente aos princípios básicos da termodinâmica clássica e quântica.

Palavras-chave: Termodinâmica; máquinas térmicas quânticas; ciclo de Otto.

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Chapter 1

Introduction

Classical thermodynamics, discussed in Chapter 2, is one of the main branches of physics that emerged in the 19th century, driven by the interest in understanding the behavior of gases and optimizing steam engines during the Industrial Revolution [1]. Famous scientists such as Sadie Carnot, Rudolf Clausius and William Thomson (Lord Kelvin) helped establishing the foundations of thermodynamics, including the concepts of conservation of energy and of entropy. Classical thermodynamics was originally used to improve heat engines and industrial processes, and over time it has been extended to areas such as chemical thermodynamics, meteorology, and energy engineering. Today, it plays a vital role in developing sustainable energy systems, improving engine efficiency and developing innovative technologies in various industrial sectors.

The Otto cycle [2], one of the most important cycles in classical thermodynamics, was proposed by Nikolaus August Otto in 1876 and is widely used in internal combustion engines such as those found in automobiles. This cycle is governed by four stages: isochoric heating (at constant volume), adiabatic expansion, isochoric cooling and adiabatic compression. The main application of this cycle describes the ideal operation of a two-stroke engine, composed of four main stages: admission, compression, expansion and exhaustion. In the intake stage, the air-fuel mixture is introduced into the combustion chamber, with isochoric heating occurring. Then, the mixture is compressed during the compression phase, increasing its temperature and pressure through an adiabatic process. Combustion occurs during the expansion phase, with the burning of the mixture generating energy and pushing the piston down, performing adiabatic expansion work. Finally, the exhaust stage removes the combustion gases from the chamber with an isochoric cooling process. The Otto cycle has been the basis for the development of efficient engines and has allowed significant advances in the automotive industry, contributing to modern mobility and sustainable transport.

Quantum thermodynamics [3], subject of the Chapter 3, emerged in the 20th century with the advent of quantum mechanics and the theory of energy quanta.

In contrast to classical thermodynamics, which focuses on the macroscopic description of systems composed of a large number of particles, quantum thermodynamics deals with systems where quantum effects are significant, such as at atomic and subatomic scales. The main differences between the theories in question reside in the nature of the studied systems and in the applicable thermodynamic laws. In quantum thermodynamics, the classical notion of well-defined states is replaced by quantum superpositions and entanglements, which leads to new emergent properties and conceptual challenges. Furthermore, classical principles such as determinism and conservation of energy can be relaxed[1] in the quantum regime, allowing for phenomena such as evaporative cooling and the violation of Bell's inequality. Quantum thermodynamics has proved to be crucial in areas such as quantum computing, where the manipulation of quantum states is essential, and opens up new perspectives for understanding the fundamental nature of matter and energy. The study of this rich intersection between thermodynamics and quantum mechanics continues to captivate and challenge scientists in their quest for a deeper understanding of physical phenomena at microscopic scales.

Quantum thermodynamics introduces an innovative perspective to the first law of thermodynamics when dealing with quantum systems. The quantum Otto cycle, an extension of the four-stroke cycle to the quantum regime, reveals unique phenomena and new approaches to heat engines on microscopic scales. In this context, "Maxwell's demon" [4] emerges as a hypothetical entity that could violate the second law of thermodynamics, separating particles of different energies in two thermal reservoirs using detailed information. In both classical and quantum thermodynamics, Maxwell's demon paradox is resolved by Landauer's principle, which states that erasing information requires energy and therefore generates heat, preserving the second law of thermodynamics in both regimes. Heisenberg's uncertainty also imposes fundamental limits on information extraction in quantum systems, contributing to the solution of Maxwell's demon paradox at microscopic scales. Exploring these concepts in quantum thermodynamics will continue to improve our understanding of quantum systems and the fundamental role of quantum mechanics in accurately describing microscopic-scale thermodynamic phenomena.

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[1] In the context of quantum thermodynamics, the "relaxation" of certain principles or phenomena of classical thermodynamics means that, at atomic and subatomic scales, the strict rules of classical thermodynamics may no longer apply or need to be reinterpreted. This is because quantum thermodynamics takes into account the discrete nature of energy levels in quantum systems, where quantum effects are significant.

Chapter 2

Classical formulation of Thermodynamics

In this chapter we discuss the basic principles of classical thermodynamics, starting with the concepts of thermodynamic equilibrium and internal energy. Then we will state the first and the second laws of thermodynamics, passing trough heat engines, focusing on Clausius formulation and, finally, the classical definition of entropy.

2.1 Energy and equilibrium

2.1.1 Thermodynamic equilibrium

Let us consider a system composed of two subsystems A and B, as shown in Fig. 2.1.

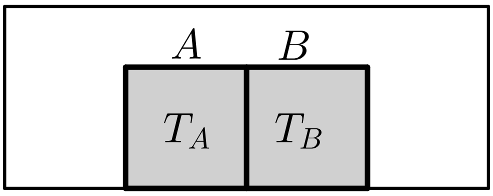

FIGURE 2.1: Illustration of the zeroth law of thermodynamics.

When the two subsystems are put into contact with each other for a long enough time and then their temperatures T_A and T_B are measured, we observe that $T_A = T_B$. Once the two subsystems reaches such a state, we say that they are in *thermal equilibrium*, and the time spent for that is called *relaxation time*.

One good application of thermal equilibrium is the measurement of the temperature using a thermometer:

- When you want to measure the temperature of something like water, for example, you must put the thermometer into contact with the vessel with water and wait until the temperature reaches a constant value (that is when the system thermometer-water reaches the thermal equilibrium). If you want to know the relaxation time, you just need to measure it with a stopwatch.

The thermal equilibrium is set up by energy exchange between two subsystems. That energy exchange due to difference of temperature is what we define as *heat*. The concept of relaxation time is clear: it defines the time that the systems spent exchanging energy until they reach the thermal equilibrium. But if you put two miscible substances —say coffee and milk— in the same vessel, it is possible to observe (almost instantly) they mixing and forming another substance. To that phenomena we give the name *diffusion* and, after we get the new substance, we say that the system got into the *diffusive equilibrium* by exchanging particles. That mixing is not necessary for the thermal equilibrium. There also exists the *mechanical equilibrium*, that is when two subsystems change the volume until it reaches to the same volume. For example, consider a vessel with a movable wall separating two different gases. These two subsystems can then freely exchange energy, volume and particles with each other, reaching equilibrium when both have the same volume.

Now we set up a table of those three types of equilibrium:

TABLE 2.1: three types of equilibrium.

Exchanged quantity	Type of equilibrium
energy	thermal
volume	mechanical
particles	diffusive

At the end of the section 2.3.5 we will show mathematically this conditions. When a system reaches the three types of equilibrium, we say that it is on the *thermodynamic equilibrium*. Actually, these cases are consequences of the so called zeroth law of thermodynamics, which states that the equilibrium state of a composite system is the one for which every net flux throughout the system vanish.

2.1.2 The ideal gas

We demand that an ideal gas obeys the following conditions:

- The particles that compose the gas are dimensionless;
- These particles do not attract/repel each other;
- All the collisions are elastic.

Such a system obeys the Clapeyron equation which establishes that

$$PV = nRT \ , \tag{2.1}$$

where P, V, n, R and T are the pressure, the volume, the number of moles, the ideal gases constant (with the value $8.31\ \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$) and the temperature of the gas, respectively.

It happens that a mole of any substance has $N_A = 6.022 \times 10^{23}$ constituents (atoms, molecules, etc.), which is known as the *Avogadro's number*. Then the number of particles in the system that contains the gas is $N = nN_A$, implying

$$PV = Nk_bT \ , \tag{2.2}$$

with $k_b \equiv R/N_A = 1.38 \times 10^{-23}\ \mathrm{J} \cdot \mathrm{K}^{-1}$ being the *Boltzmann's constant.*

2.1.3 The internal energy

The average energy of one particle is[1] $fk_bT/2$, where $f \in \mathbb{N}$ is the number of degrees of freedom of the particle. Considering a system composed by N identical and non-interacting particles (ideal gas), the total energy of the system is the sum of all the mean energies of each particle

$$U \equiv \frac{f}{2} Nk_bT \ . \tag{2.3}$$

Notice that our formulation describes a macroscopic system, that can be viewed as an agglomerate of an enormous number of electrons and nuclei, interacting with complex but definite forces in wich the energy conservation principle applies. Then, we conclude that macroscopic systems have definite and precise energies, subject to a definite conservation principle.

That is, we now accept that the existence of well-defined energies in thermodynamic systems is a macroscopic manifestation of a conservation law that is complex, tested with extreme precision, and apparently has complete generality at the atomic level. The justification for the existence of the thermodynamic energy function described in this paragraph is quite different from the historical thermodynamic approach.

Since thermodynamics was largely developed before the atomic hypothesis was accepted, the existence of a conservative macroscopic energy function had to be proved by purely macroscopic means. Count Rumford took an important step in

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[1] The derivation of this expression can be found in [2]

this direction in 1798 when he observed certain thermal effects associated with the boring of brass cannons. Sir Humphry Davy, Sadi Carnot, Robert Mayer and finally James Joule led Rumford's initial efforts to their logical realization. The history of the concept of heat as a form of energy transfer is unparalleled, a case study in the tortuous development of scientific theory, an illustration of the almost insurmountable inertia of accepted physics, and a magnificent story of human ingenuity applied to science. A subtle and abstract question.

Once only differences of energy, rather than absolute values of the energy, have physical significance, either at the atomic level or in macroscopic systems, it is conventional therefore to adopt some particular state of a system as our reference. Let us consider an equilibrium state with an arbitrary energy U_0. If we evolve our system by an adiabatic path (section 2.2.3) we end up in a new equilibrium state with energy U_F and then we define the *internal energy* of the system as

$$U \equiv U_F - U_0 = \int_\Gamma \vec{F} \cdot d\vec{\ell}\,, \tag{2.4}$$

where $\vec{F}$ is the applied force and $d\vec{\ell}$ is the differential line element of the path Γ. Therefore, we are defining the internal energy based on the work and energy theorem.

For the ideal gas, we take Eq. (2.3) as the internal energy.

2.2 First law of thermodynamics

We start this section by defining some important quantities

- **Temperature** (T): physical quantity that measures the average level of agitation of the particles that compose a system;
- **Heat** (Q): Energy flux between two or more subsystems, caused by difference of temperature between them;
- **Work** (W): Any exchange of energy that isn't heat.

Figure 2.2 shows a generic system subject to energy flux

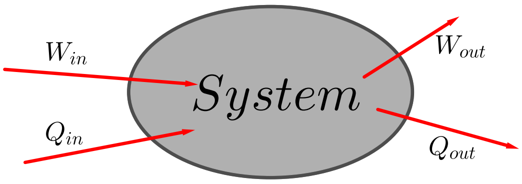

FIGURE 2.2: energy flux on a system.

Following the direction of the fluxes indicated in Fig. 2.2, we will adopt the following signal convention for the energies fluxes

$$\begin{cases} W_{in}, Q_{in} \geq 0 \\ W_{out}, Q_{out} \leq 0 \end{cases} . \tag{2.5}$$

Since we have two types of energy in our system, we postulate the first law of thermodynamics in the macroscopic form as

$$\Delta U \equiv Q + W \ , \tag{2.6}$$

which takes the following infinitesimal form

$$\mathrm{d}U = \delta Q + \delta W \ , \tag{2.7}$$

where we used the notation δ instead of d because heat and work are already variations of energy and thus they are not exact differential forms. A further discussion about that equality between exacts and non-exacts differential forms can be found on page 33 of Ref. [5].

2.2.1 Mechanical work on a ideal gas

Before we get into the mechanical work, we need to define a *quasistatic* process

- A quasistatic process, also called *reversible process*, is a kind of thermodynamic process that occurs at a very slow rate (infinite time), such that the system remains in a state of thermodynamic equilibrium throughout the entire process. That means that the system is always very close to being in equilibrium, and any changes that occur happen so slowly that the system can continuously adjust to maintain the equilibrium.

Now let us consider a cylinder with one wall that can move, containing an ideal gas and with a force $\vec{F}$ acting on that wall[2], as illustrated in Fig. 2.3:

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[2] Here we are considering that the compression occurs in the quasistatic way.

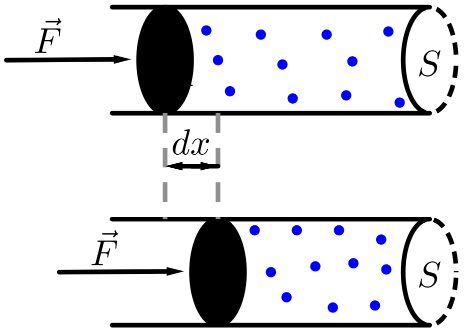

FIGURE 2.3: Compression of an ideal gas contained in a cylindrical vessel of cross area S.

Considering $\mathrm{d}x$ as the infinitesimal change in the position of the wall, the microscopic mechanical work on the system is

$$\delta W = -F dx \; , \tag{2.8}$$

where the minus signal appears because of our convention defined in Eq. (2.5) since the change in the $x-$position of the wall implies a negative change of the volume of the cylinder. We have then

$$\delta W = -PSdx \; , \tag{2.9}$$

$$\Rightarrow \; \delta W = -PdV \; , \tag{2.10}$$

where dV is the infinitesimal change in the volume of the cylinder.

Thus, the macroscopic form of the mechanical work is given by

$$W = -\int PdV \; . \tag{2.11}$$

2.2.2 Work of an reversible isothermal process

Consider that we have a system on the initial state with volume V_0 that evolves to a final state with volume rV_0 through a quasistatic process that does not change its temperature T. Then, the related work of that process is

$$W = -\int PdV = -Nk_bT \int_{V_0}^{rV_0} \frac{dV}{V} \; , \tag{2.12}$$

$$W = Nk_bT \ln \left(\frac{1}{r} \right) \; . \tag{2.13}$$

Notice that, if $r > 1$ we have an *isothermal expansion* and thus the work is done *by* the system because $1/r < 1$ implies $\ln(1/r) < 0$ and consequently $W < 0$. In the same way, if $r < 1$, we have an *isothermal compression* with the work being done *on* the system and $W > 0$.

2.2.3 Reversible adiabatic process

An adiabatic process is a thermodynamic transformation such that there is no heat involved. Assuming a quasistatic and adiabatic process, the first law of thermodynamics, $\mathrm{d}U = \delta Q + \delta W$, can be written as

$$\mathrm{d}U = -P\mathrm{d}V \ . \tag{2.14}$$

Since the process is quasistatic, we must have $\delta W = -pdV$ as the mechanical work (that can be extracted or applied to the system). Considering that our system is composed of some ideal gas, the infinitesimal change in the internal energy is $\mathrm{d}U = fNk_b dT/2$ where $\mathrm{d}T$ is the infinitesimal change of the temperature of the system. For any quasistatic and adiabatic processes, we have that

$$\frac{f}{2}Nk_b dT = -PdV \ . \tag{2.15}$$

We know from Clapeyron's equation that $P = Nk_bT/V$ and thus

$$\Rightarrow \ \frac{f}{2}\frac{dT}{T} = -\frac{dV}{V} \ . \tag{2.16}$$

Integrating Eq. (2.16) over some reversible path $(T_0, V_0) \mapsto (T_F, V_F)$, where the indices "0" and "F" labels, respectively, the initial and final states, we obtain

$$\frac{f}{2}\ln\left(\frac{T_F}{T_0}\right) = \ln\left(\frac{V_0}{V_F}\right) \ , \tag{2.17}$$

$$\Rightarrow \ \ln\left(\frac{T_F}{T_0}\right)^{f/2} = \ln\left(\frac{V_0}{V_F}\right) \ , \tag{2.18}$$

$$\Rightarrow \ T_F V_F^{2/f} = T_0 V_0^{2/f} \ , \tag{2.19}$$

that allows us to write

$$TV^{2/f} = \text{constant} \ . \tag{2.20}$$

Since $PV = Nk_bT$, we have that

$$PV^{1+2/f} = \text{constant} \ , \tag{2.21}$$

from where we define the *adiabatic coefficient* as $\gamma \equiv 1 + 2/f$ and then it is possible to rewrite Eqs. (2.20) and (2.21) as

$$\begin{cases} PV^{\gamma} = \text{constant} \\ TV^{\gamma-1} = \text{constant} \end{cases} . \tag{2.22}$$

2.2.4 Work of an reversible adiabatic process

The equation of the adiabatic transformation is

$$PV^{\gamma} = \xi \ , \tag{2.23}$$

where ξ is a constant.

Suppose that a system evolves under a quasistatic adiabatic process, starting with pressure P_0 and volume V_0 and finishing with pressure ϵP_0 and volume rV_0. The related work of this process is

$$W = -\int P dV = -\xi \int_{V_0}^{rV_0} V^{-\gamma} dV \ , \tag{2.24}$$

$$\Rightarrow \ W = \frac{\xi r^{1-\gamma} V_0^{1-\gamma} - \xi V_0^{1-\gamma}}{\gamma - 1} \ . \tag{2.25}$$

We can write $\xi = P_0 V_0^{\gamma}$ or $\xi = \epsilon r^{\gamma} P_0 V_0^{\gamma}$ and, consequently,

$$\epsilon r^{\gamma} = 1 \ . \tag{2.26}$$

Backing to Eq. (2.25), we have that

$$W = \frac{P_0 V_0}{\gamma - 1}(\epsilon r - 1) \ , \tag{2.27}$$

or

$$W = \frac{P_0 V_0}{\gamma - 1}(r^{1-\gamma} - 1) \ . \tag{2.28}$$

Since $\gamma = 1 + 2/f > 1$, then $1 - \gamma < 0$. From this follows that $r > 1$ implies $W < 0$ and $r < 1$ implies $W > 0$.

2.3 Entropy and the Second law of thermodynamics

The first law states the conservation of energy, as we have seen. Any process for which the total energy is constant is compatible with the first law. If a given process occurs in a certain direction or temporal sequence, conserving energy at each instant, nothing would prevent, according to the first law, that it occurs in the opposite direction[3], that is, the process would be reversible. However, experience shows that the processes observed at the macroscopic scale tend to occur in only one direction, that is, they are irreversible. An example is the *free expansion* of a ideal gas:

- Initially, we let the gas separated by a wall from an evacuated chamber and then we make a hole in the wall, letting the gas freely expand to fill the whole available space, as shown in Fig. 2.4. Once the isn't pushing anything, it can't do any work. In the same way, no heat flowed into or out of the gas. Therefore, the first law becomes $\Delta U = 0$. Once this system reached the equilibrium condition, there is no reason for the gas go back to its initial state before the expansion.

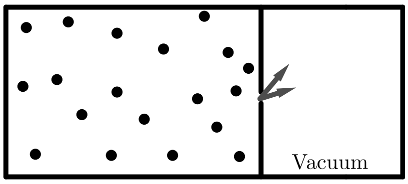

FIGURE 2.4: free expansion of a gas into vacuum.

In this section we will discuss the second law of thermodynamics and define the concept of entropy. Such fundamental law can be formulated in many distinct, but equivalent ways and we give two of them bellow.

- Kelvin Statement **(K)**: It is impossible to execute a process such that the only effect is to remove heat from a reservoir and produce an equivalent quantity of work;

- Clausius Statement **(C)**: It is impossible to execute a process such that the only effect is to transfer heat from a colder system to a hotter system.

Notice that the word "only" implies a cyclic process. If we don't state this, the heat flow is perfectly possible.

---

[3] Inverting the temporal sequence

2.3.1 The equivalency of the two statements

Heat engine

Heat engines are machines that produce work from a temperature difference between two reservoirs, as depicted in Fig. 2.5. In this chapter we will focus on the work, power and efficiency of classical thermodynamic engines ruining in cycles, using the first and second laws of thermodynamics. We then apply these concepts to the Otto engine.

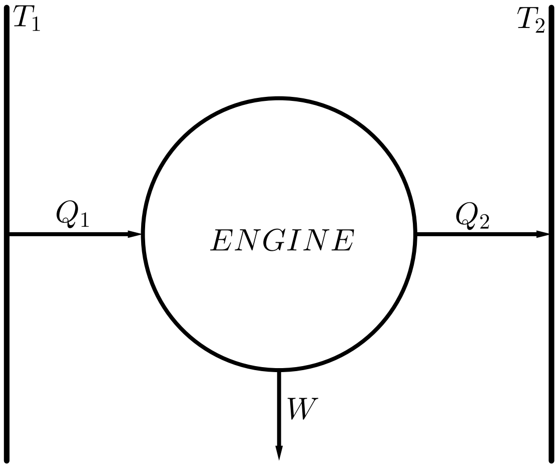

FIGURE 2.5: Overview of a heat engine. The engine operates between two heat environments at temperatures T_1 and T_2, respectively. Heat flows through the engine while work is extracted from it. The first law of thermodynamics says that $W = Q_1 - Q_2$, while the second law states that Q_2 cannot vanish.

Work, efficiency and power of thermodynamic cycles

On a cycle, we have that the initial point and the final point are the same, thus the internal energy at the beginning is equal to the internal energy at the end, thus implying

$$W = -Q \, , \tag{2.29}$$

from the first law of thermodynamics.

The efficiency of any machine is defined by

$$\eta \equiv \frac{\text{benefit}}{\text{cost}} \, . \tag{2.30}$$

Once our heat engines are used to turn heat into work, the efficiency is given by

$$\eta = \frac{|W|}{Q_1} \, , \tag{2.31}$$

where $|Q| = Q_1 - Q_2$ and, from Eq. (2.29), $|W| = |Q|$, resulting in

$$\eta = 1 - \frac{Q_2}{Q_1} \,. \tag{2.32}$$

Suppose that our engine realizes a number k of stages in the reversible regime and each stage occurs in an infinite time. The power of the cycle can be written as

$$\mathbb{P} = \sum_{i=1}^{k} \frac{|W_i|}{\Delta t_i} \,. \tag{2.33}$$

Since $\Delta t_i \to \infty$, we have that

$$\mathbb{P} = 0 \,. \tag{2.34}$$

We can conclude that a reversible engine will provide zero power.

Refrigerator

- A refrigerator is a machine that removes the heat Q_2 from a cold reservoir at temperature T_2 and throws away the heat Q_1 into a hot reservoir at temperature $T_1 > T_2$. Since we can not do this process spontaneously, we need to inject some work on the refrigerator, as shown in Fig. 2.6.

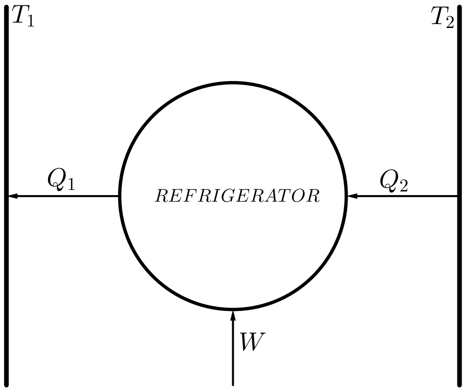

FIGURE 2.6: Overview of a refrigerator.

Since this process is cyclic, we have $\Delta U = 0$ and then

$$W + Q_2 - Q_1 = 0 \;\Rightarrow\; Q_1 = W + Q_2 \,. \tag{2.35}$$

The efficiency of the refrigerator is

$$\eta = \frac{Q_2}{|W|} = \frac{Q_2}{Q_1 - Q_2} \,, \tag{2.36}$$

$$\eta = \frac{1}{Q_2/Q_1 - 1} \, . \tag{2.37}$$

The equivalence

Finally, we are going to show the equivalence between **(K)** and **(C)** statements.

- **(K)** $\Rightarrow$ **(C)**: if **(K)** $\nRightarrow$ **(C)**, a real engine, E, could be coupled to a "magic refrigerator", MR, once **(C)** would not be valid. This MR would return the heat Q_2 to the hot reservoir and the consequence should be remove the heat $Q_1 - Q_2$ from the hot reservoir and produce an equivalent quantity of work, that means that there exists a "magic engine", ME, and thus **(K)** is violated, as shown in Fig. 2.7. Consequently, we have that **(K)** $\Rightarrow$ **(C)**.

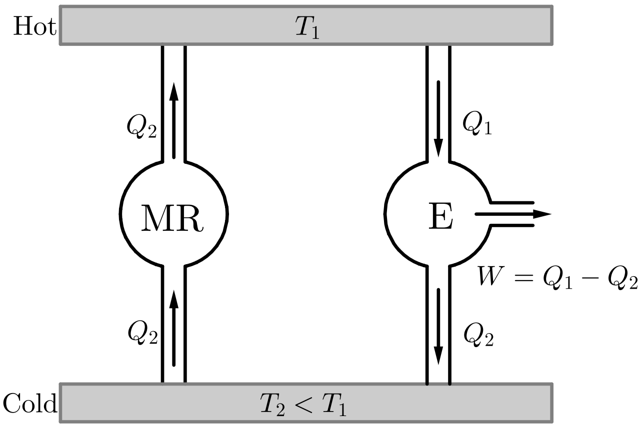

FIGURE 2.7: **(K)** $\Rightarrow$ **(C)**.

- **(C)** $\Rightarrow$ **(K)**: if **(C)** $\nRightarrow$ **(K)**, a real refrigerator, R, could be coupled to a "magic engine", ME, once **(K)** would not be valid. This ME should produce an quantity of work equal to $Q_1 - Q_2$ and this work would charge the refrigerator R. The result of this process should be the total flow of the heat Q_2 from the cold to the hot reservoir, without any other effect. Consequently, the refrigerator wold be a "magic refrigerator", violating **(C)**, according to the Fig. 2.8. We have then **(C)** $\Rightarrow$ **(K)** and thus **(K)** $\Leftrightarrow$ **(C)**.

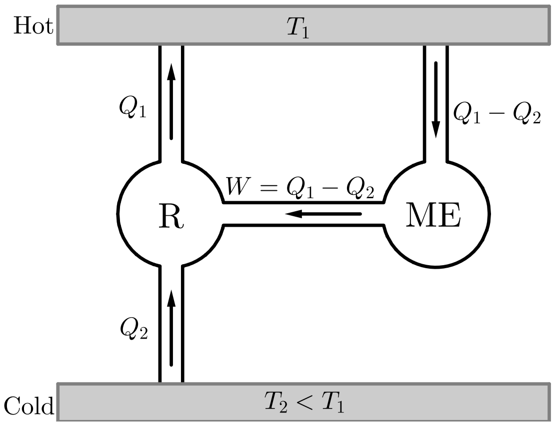

FIGURE 2.8: **(C)** ⇒ **(K)**.

2.3.2 The Carnot Cycle

We can now focus on the following problem: given a hot and a cold reservoir, what is the maximum efficiency we can get from a heat engine that operates between these two reservoirs?

For maximum efficiency, the thermodynamic processes carried out by the heat engine need to be reversible. Otherwise, energy gains and losses at each step of the thermodynamic cycle will decrease efficiency. Since heat conduction is irreversible[4], the system used can only exchange heat with the reservoir when they are at the same temperature.

Therefore, the absorption of heat Q_1 from the hot reservoir by the heat engine must occur isothermally, as well as the rejection of heat Q_2 from the machine to the cold reservoir. Furthermore, in order to obtain the maximum efficiency of the motor, the stages where temperature variations occur must occur under adiabatic processes, where there is no heat exchange. A heat engine that works under these conditions is called a Carnot engine. Fig. 2.9 illustrates the *Carnot cycle*:

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[4] If two bodies of different temperatures come into thermal contact, transferring heat by conduction, the corresponding thermal energy cannot be recovered in a cyclic process, as this would imply the transfer of heat from a cold to a hot body, violating **(C)**.

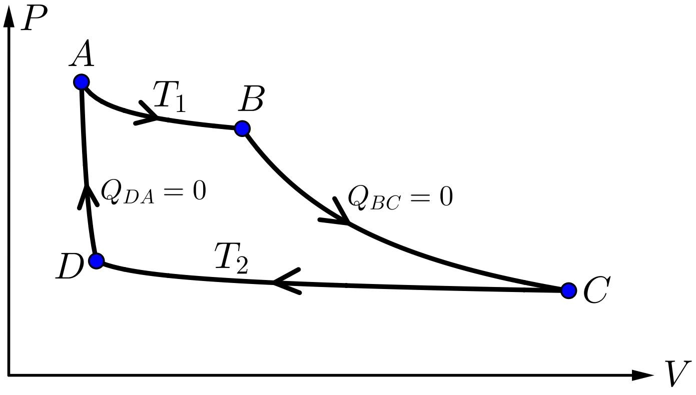

FIGURE 2.9: Carnot diagram.

We can now state the *Carnot Theorem*:

(a) For a given hot and cold reservoirs, there no exists a heat engine that is more efficient than the Carnot engine.

(b) Every Carnot engine operating between the same reservoirs have the same efficiency.

The efficiency of a heat engine is $\eta = 1 - Q_2/Q_1$, as shown in Eq. (2.32). We have that $Q_1 = |W_{AB}|$ and $Q_2 = |W_{CD}|$:

$$W_{CD} = -\int_{V_C}^{V_D} \frac{Nk_bT_2}{V} dV = Nk_bT_2 \ln\left(\frac{V_C}{V_D}\right) > 0 \,. \tag{2.38}$$

$$W_{AB} = -\int_{V_A}^{V_B} \frac{Nk_bT_1}{V} dV = Nk_bT_1 \ln\left(\frac{V_A}{V_B}\right) < 0 \,. \tag{2.39}$$

On the isothermal paths, we have

$$P_AV_A = P_BV_B \;\Rightarrow\; \frac{V_A}{V_B} = \frac{P_B}{P_A} \,, \tag{2.40}$$

and

$$P_CV_C = P_DV_D \;\Rightarrow\; \frac{V_C}{V_D} = \frac{P_D}{P_C} \,. \tag{2.41}$$

On the adiabatic paths, we have

$$P_BV_B^\gamma = P_CV_C^\gamma \;\Rightarrow\; \left(\frac{V_B}{V_C}\right)^\gamma = \frac{P_C}{P_B} \,, \tag{2.42}$$

and

$$P_DV_D^\gamma = P_AV_A^\gamma \;\Rightarrow\; \left(\frac{V_A}{V_D}\right)^\gamma = \frac{P_D}{P_A} \,, \tag{2.43}$$

and thus

$$\left(\frac{V_B}{V_A}\frac{V_D}{V_C}\right)^{\gamma} = \frac{P_C}{P_D}\frac{P_A}{P_B} \Rightarrow \frac{P_A}{P_B} = \frac{P_D}{P_C} \ . \tag{2.44}$$

Since $Q_1 = Nk_bT_1\ln(P_A/P_B)$ and $Q_2 = Nk_bT_2\ln(P_D/P_C)$, we have that the efficiency of the Carnot cycle is given by

$$\eta_c = 1 - \frac{T_2}{T_1} \ , \tag{2.45}$$

that means that we must have $Q_2/Q_1 = T_2/T_1$ for the maximum efficiency.

2.3.3 The Clausius theorem

We saw in the previous subsection that a Carnot engine operating between two reservoirs at temperatures T_1 and T_2 respect the relation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \ , \tag{2.46}$$

with $Q_{1,2} > 0$ being the amounts of heat supplied to the system by the hot reservoir and supplied by the system to the cold reservoir, respectively. When we model the heat engines, we take such positive values for Q to be more convenient. However, in this section we will refer to heats supplied to the system and, therefore, we will make the exchange $Q_2 \to -Q_2$, in such way that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \sum_{\text{RCC}} \frac{Q}{T} = 0 \ , \tag{2.47}$$

where RCC means "Reversible Carnot Cycle".

The Clausius theorem generalizes Eq. (2.47) for any reversible cycle: let us consider a reversible path Γ and four points a, b, A and B on the $P \times V$ diagram, as shown in Fig. 2.10

By construction, we are taking a small portion of the path Γ and covering it with two adiabatic and an isotherm reversible curves such that the area under the path is equal to the area bounded by the isotherms and the adiabatic curves. This small path replacement is equivalent to cover our path with a reversible Carnot cycle. Once the heat on the adiabatic curves is zero, we have that

$$Q_{AB} = Q_{ab} \ . \tag{2.48}$$

Now we can threat a reversible cycle Γ using the idea of the path replacement. Looking at Fig. 2.11, we can cover the full cycle with a collection of adiabatic and isotherm reversible curves such that the area of the cycle (that is numerically equal to the work of the cycle) is divided in a set of Carnot engines.

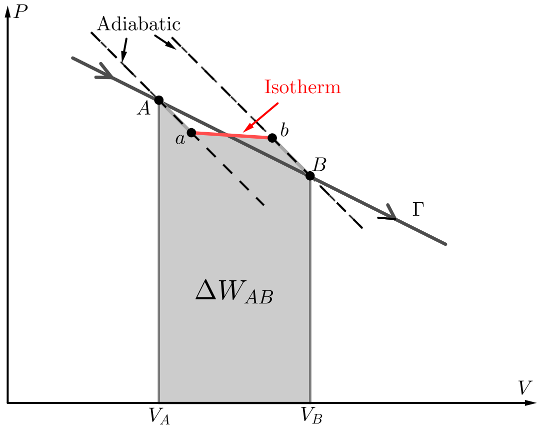

FIGURE 2.10: path replacement.

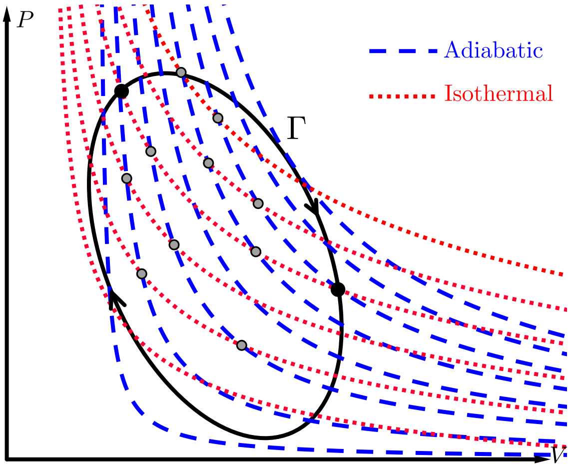

FIGURE 2.11: path replacement in the full cycle.

For each Carnot cycle covering Γ, we have that

$$\sum_{\text{RCC}} \frac{\Delta Q}{T} = 0 \,, \tag{2.49}$$

and for small portions of the cycle:

$$\lim_{\Delta Q \to 0} \sum_{\text{all cycles}} \left\{ \sum_{\text{RCC}} \frac{\Delta Q}{T} \right\} = \oint_{\Gamma} \frac{\delta Q}{T} \,, \tag{2.50}$$

$$\Rightarrow \oint_{\Gamma} \frac{\delta Q}{T} = 0 \,, \text{ for } \Gamma \text{ reversible.} \tag{2.51}$$

The physical interpretation of the path replacement of Γ by adiabatics and isotherms is that a system operating cyclically gains heat from the Carnot engine and converts it to work and thus both cycles get back to the initial state. The only resulting effect in this system is that the engine operating cyclically removes a quantity of heat from the Carnot engine and produces a equivalent quantity of work. In order to obey the Second Law, this path replacement is only possible if

$$\oint_\Gamma \frac{\delta Q}{T} \leq 0 \, , \tag{2.52}$$

and, if Γ is irreversible, then

$$-\oint_\Gamma \frac{\delta Q}{T} \leq 0 \, , \tag{2.53}$$

that results in

$$\begin{cases} \oint_\Gamma \dfrac{\delta Q}{T} = 0 \, , \text{ for } \Gamma \text{ reversible} \\ \\ \oint_\Gamma \dfrac{\delta Q}{T} \leq 0 \, , \text{ for } \Gamma \text{ irreversible} \end{cases} \, . \tag{2.54}$$

Now we define a physical quantity called *entropy*

$$dS \equiv \frac{\delta Q}{T} \, , \tag{2.55}$$

$$\Delta S = S_B - S_A = \int_A^B \frac{\delta Q}{T} \, , \tag{2.56}$$

with A and B being the labels of two different equilibrium tates. This physical quantity is usually interpreted as the *degree of disorder* of the system or *the thermal energy that is unavailable to be converted into work.*

2.3.4 The principle of increasing entropy

Equations (2.54) establishes the entropy changes for reversible and irreversible cycles, with T being the temperature of a body that transfers heat δQ to the system of interest. When the integral of $\delta Q/T$ vanishes, there is no thermodynamic reason why the path Γ is irreversible, so we will consider

$$\oint_\Gamma \frac{\delta Q}{T} < 0 \, , \text{ for } \Gamma \text{ irreversible.} \tag{2.57}$$

Now consider two paths R and I, reversible and irreversible, respectively, as shown in Fig. 2.12, linking two states of thermodynamic equilibrium. We represent the irreversible path by dotted lines, as it does not need to pass through intermediate states of equilibrium.

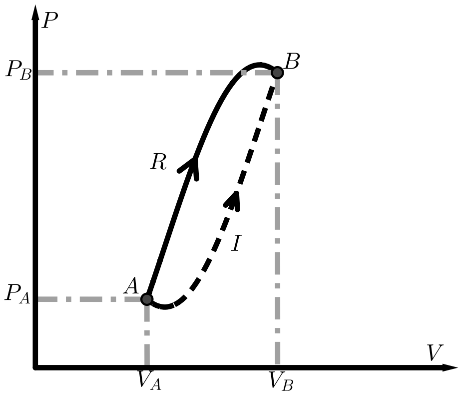

FIGURE 2.12: Reversible and irreversible paths

The convolution $\Gamma = I * (-R)$ is an irreversible cycle and thus

$$\oint_\Gamma \frac{\delta Q}{T} = \int_{(-R)} \frac{\delta Q}{T} + \int_I \frac{\delta Q}{T} \,, \tag{2.58}$$

$$\Rightarrow \left[\int_B^A \frac{\delta Q}{T}\right]_{\text{reversible}} + \int_I \frac{\delta Q}{T} < 0 \,, \tag{2.59}$$

$$\Rightarrow (S_A - S_B) + \int_I \frac{\delta Q}{T} < 0 \,, \tag{2.60}$$

$$\Rightarrow (S_B - S_A) - \int_I \frac{\delta Q}{T} > 0 \,, \tag{2.61}$$

$$\Rightarrow \Delta S > \int_I \frac{\delta Q}{T} \,. \tag{2.62}$$

If the path I were reversible, the expression (2.59) would be the same, but set to zero. We have then

$$\Delta S \geq \int_I \frac{\delta Q}{T} \,, \tag{2.63}$$

where equality holds if the path I is reversible.

If the system is isolated, $\delta Q = 0$ and then

$$\Delta S_{\text{system}} \geq 0 \,, \tag{2.64}$$

that is the principle of increasing entropy.

Equilibrium between two subsystems

Consider a system composed by one vessel with a dimensionless and movable wall dividing two subsystems A and B, as shown in Fig. 2.13. Assuming that this wall doesn't allows particles exchange, we have that

$$\begin{cases} dS_A = \frac{1}{T_A} dU_A + \frac{P_A}{T_A} dV_A \\ dS_B = \frac{1}{T_B} dU_B + \frac{P_B}{T_B} dV_B \end{cases} , \tag{2.65}$$

where we are combining $\delta Q = TdS$ with the first law.

Our entire system have energy $U = U_A + U_B$, and we know from conservation of energy that

$$dU = 0 \ \Rightarrow \ dU_B = -dU_A \ . \tag{2.66}$$

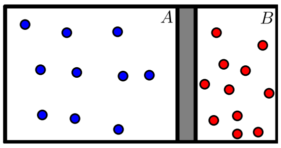

FIGURE 2.13: vessel divided in two subsystems by a movable wall.

Under the condition of equilibrium, we must have the maxium amount of entropy and, for that:

$$dS = d(S_A + S_B) = 0 \ . \tag{2.67}$$

The volume $V = V_A + V_B$ of the system does not change, and thus $dV_A = -dV_B$. In this way, if we sum equations 2.65 we have:

$$d(S_A + S_B) = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A = 0 \ , \tag{2.68}$$

that holds if and only if

$$\begin{cases} T_A = T_B \\ P_A = P_B \end{cases} . \tag{2.69}$$

If the wall allows the subsystems A and B to exchange particles, the infinitesimal work is $\delta W = -PdV + \mu dN$, where μ is the *chemical potential*, that is the physical quantity that checks the diffusive equilibrium. With this modification, our system is in thermodynamical equilibrium if and only if

$$\begin{cases} T_A = T_B \\ P_A = P_B \\ N_A = N_B \end{cases} . \tag{2.70}$$

With the condition $N_A = N_B$, Clapeyron's equation leaves us to

$$V_A = V_B \,. \tag{2.71}$$

Thus, considering that the state of thermodynamical equilibrium leaves us to the condition of maximum entropy, we recover the definitions of thermal, diffusive and mechanical equilibrium discussed in 2.1.1.

2.4 The reversible Otto Cycle

2.4.1 Otto cycle

The Otto cycle is an thermodynamic cycle that describes how heat engines turn fuel into motion. This cycle is composed of two adiabatic and two isochoric curves and describes how internal combustion engines, like cars, work. The Fig. 2.14 (by *Thayna Alves, FAV-UFG*) shows an example of a Otto engine and Fig. 2.15 illustrates the $P \times V$ diagram of the cycle.

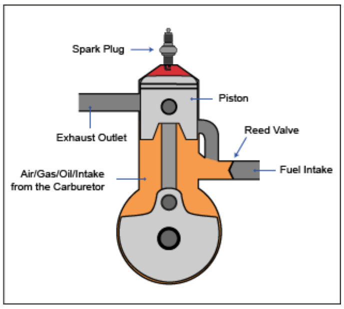

FIGURE 2.14: Two-stroke engine.

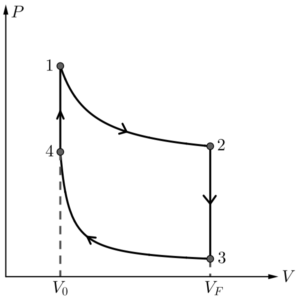

FIGURE 2.15: $P \times V$ diagram of Otto Cycle.

Looking at the diagram in Fig. 2.15, we have[5]:

- $(1 \rightarrow 2)$: Adiabatic expansion $\Rightarrow\ T_1 V_0^{\gamma-1} = T_2 V_F^{\gamma-1}\ (*)$;
- $(2 \rightarrow 3)$: Isochoric cooling $\Rightarrow\ Q_2 = \mathbb{C}_V (T_3 - T_2)$;
- $(3 \rightarrow 4)$: Adiabatic compress $\Rightarrow\ T_4 V_0^{\gamma-1} = T_3 V_F^{\gamma-1}\ (**)$;
- $(4 \rightarrow 1)$: Isochoric heating $\Rightarrow\ Q_1 = \mathbb{C}_V (T_1 - T_4)$.

---

[5] The heat flows in the stages $(2 \rightarrow 3)$ and $(4 \rightarrow 1)$ holds because $\mathbb{C} \equiv \dfrac{dQ}{dT}$, where $\mathbb{C}$ is the *heat capacity* of the system, that we are assuming as a constant. Once we have two isochoric paths, we label the heat capacity with the index "V".

Subtracting $(**)$ from $(*)$, we have:

$$\frac{T_2 - T_3}{T_1 - T_4} = \left(\frac{V_0}{V_F}\right)^{\gamma-1} , \tag{2.72}$$

defining the *compressibility factor* $r \equiv V_F/V_0$, the Eq. (2.72) becomes

$$\frac{T_2 - T_3}{T_1 - T_4} = r^{1-\gamma} . \tag{2.73}$$

The efficiency of the cycle is

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\mathbb{C}_V |T_3 - T_2|}{\mathbb{C}_V (T_1 - T_4)} , \tag{2.74}$$

$$\Rightarrow \eta = 1 - \frac{T_2 - T_3}{T_1 - T_4} . \tag{2.75}$$

Putting the Eq. (2.73) into Eq. (2.75), we end up with

$$\eta = 1 - r^{1-\gamma} , \tag{2.76}$$

that is the efficiency of the Otto cycle. The power of the cycle is zero, as discussed in section before.

We can make a $T \times S$ diagram of the Otto cycle[6]. Once the adiabatic curves don't allows heat flows, the entropies in the paths $1 \to 2$ and $3 \to 4$ (Fig. 2.16) are constant[7].

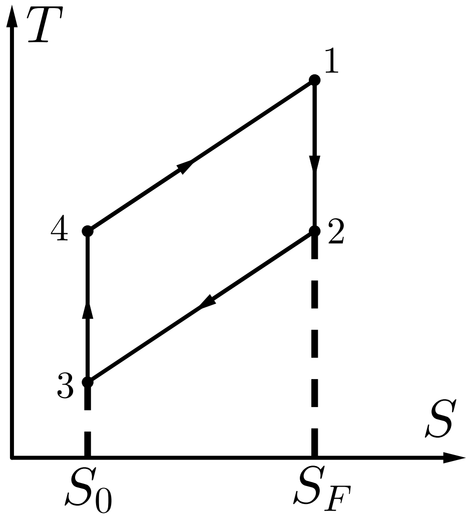

FIGURE 2.16: $T \times S$ diagram of the Otto cycle.

---

[6] This one is equivalent to the $P \times V$ diagram.

[7] This holds by the classical definition $\delta Q = TdS$.

Chapter 3

Quantum Otto Engine

The classic Otto cycle is the cornerstone of traditional thermodynamics, which describes the behavior of a four-stroke heat engine in terms of macroscopic principles. Quantum Otto cycles, on the other hand, go beyond this point of view by considering quantum interactions between particles and energy on a microscopic scale. While classical loops provide a thorough understanding of internal combustion engines, quantum loops add complexity to the analysis and emphasize the need to evaluate quantum phenomena occurring in thermal systems. This broader approach is crucial for optimizing the performance of heat engines where quantum effects are critical, and opens new perspectives on energy efficiency at the microscopic level.

In this chapter we are going to set up some basic principles of the evolution of a thermodynamic cycle in quantum mechanics, starting with the description of the system by a density operator. We proceed with the first law and finish with the quantum adiabatic evolution. Finally, we will study the quantum Otto cycle and derive its efficiency.

3.1 Density operators

People often resort to concepts of probability when they have incomplete information about a system. For example, we know that photons emitted by natural light sources can assume any polarization state with equal probability. Likewise, the probability that a system in thermodynamic equilibrium at temperature T has energy E_n is proportional to e^{-E_n/k_bT}. More generally, the incomplete information one has about a system is usually represented in quantum mechanics as follows: the state of this system may be either the state $|\varphi_1\rangle$ with probability p_1 or the state $|\varphi_2\rangle$ with probability p_2, etc. Obviously:

$$\sum_k p_k = p_1 + p_2 + \cdots = 1 \ . \tag{3.1}$$

We then say that we are dealing with a *statistical mixture* of states $\{|\varphi_k\rangle\}$ with probabilities $\{p_k\}$. Now let's see what happens to the predictions of the measurements made on this system. If the state of the system is $|\varphi_k\rangle$, we can use the assumptions of quantum mechanics to determine the probability of obtaining a certain measurement outcome. Since this possibility ($|\varphi_k\rangle$) has probability p_k, it is clear that the result obtained must be weighted with this probability and summed over different values of k (i.e. all states of the statistical mixture).

Comments:

(i) The states $\{|\varphi_k\rangle\}$ are not necessarily orthogonal. However, they can always be chosen normalized, that is what we are going to assume.

(ii) It must be noted that in the present case, the probabilities intervene on two different levels:

- first, in the initial information about the system[1];
- then, when the postulates concerning the measurement are applied[2].

Therefore, two quite different reasons make it necessary to introduce probability at these two levels: the incompleteness of the initial information about the state of the system (which is also foreseen in classical mechanics) and the uncertainty associated with the measurement process.

(iii) A system described by a statistical mixture of states must not be confused with a system whose state $|\Psi\rangle$ is a linear superposition of states:

$$|\Psi\rangle = \sum_k c_k \, |\varphi_k\rangle \ , \tag{3.2}$$

where we did consider $\{|\varphi_k\rangle\}$ as an orthonormal basis of Hilbert space. It is often said in quantum mechanics, when the state vector is that one given in Eq. (3.2), that *the system has a probability* $|c_k|^2$ *of being in the state* $|\varphi_k\rangle$. For example, if we want to calculate the probability $\mathscr{P}(a_n)$ of the measurement of the quantity a_n (non-degenerated) associated to a observable A, quantum mechanics says that

$$\mathscr{P}(a_n) = |\, \langle\psi_n|\Psi\rangle \,|^2 \ , \tag{3.3}$$

---

[1] Here we assume that the state vector is completely known. In this case, all but one probabilities p_k are zero

[2] This leads to probabilistic predictions even when the initial state of the system is perfectly known.

where $|\psi_n\rangle$ is the normalized autoket of A associated with the value a_n.
We have then

$$\mathscr{P}(a_n) = \left[\sum_k c_k \langle\psi_n|\varphi_k\rangle\right]\left[\sum_j c_j \langle\psi_n|\varphi_j\rangle\right]^* \ , \tag{3.4}$$

$$\Rightarrow \ \mathscr{P}(a_n) = \sum_{j,k} c_k c_j^* \langle\psi_n|\varphi_k\rangle \langle\varphi_j|\psi_n\rangle \ , \tag{3.5}$$

from where we define an *interference operator* $\mathscr{I} \equiv \sum\limits_{j,k} c_k c_j^* |\varphi_k\rangle\!\langle\varphi_j|$ and thus

$$\mathscr{P}(a_n) = \langle\mathscr{I}\rangle_n \ , \text{ where } \langle \quad \rangle_n \equiv \langle\psi_n| \quad |\psi_n\rangle \ . \tag{3.6}$$

If we want to be more specific, we have to understand that if we take a set of measurements on a complete set of commuting observables with $|\varphi_k\rangle$ as eigenvector, the probability of finding the set of eigenvalues corresponding to that state is $|c_k|^2$. However, we know that the fact that the system is in the same state $|\Psi\rangle$ according to Eq. (3.2) is not simply equivalent to the fact that the system has the probability $|c_1|^2$ of being in states $|\varphi_1\rangle$ and $|c_2|^2$ to locate the fact that for $|\varphi_2\rangle$, etc. There are usually interference effects between these states (due to cross terms of the type $c_k c_j^*$), which are very important in quantum mechanics.

Thus, we see that, in general, it is not possible to describe the statistical mixture by an "average state vector", which would be a superposition of states $|\varphi_k\rangle$. As we have already pointed out, we can never obtain the interference term between different states $|\varphi_k\rangle$ of the statistical mixture when forming the *weighted sum* of probabilities.

3.1.1 The pure state case

Before examining this general case, let us first examine a simple case where the state of the system is called a "pure state". We will show that characterizing a system by a state vector is equivalent to characterizing it by a specific operator (the density operator) acting on the same Hilbert space. The usefulness of this operator will become clear in the next subsection, where we show that almost all formulations involving this operator and derived for the pure case are still valid for the description of the statistical mixture of states.

Description by a state vector

Consider a complete and orthonormal basis for the Hilbert space as $\{|k\rangle\}$. The state vector of a system can be described in this basis:

$$|\Psi(t)\rangle = \sum_k c_k(t)\,|k\rangle \ . \tag{3.7}$$

The coefficients $c_k(t)$ have a constraint

$$\sum_k |c_k(t)|^2 = 1 \ , \tag{3.8}$$

that holds by the normalization of the state. If A is an observable, with matrix elements $A_{ij} = \langle i|\,A\,|j\rangle$, the expectation value of A at the instant t is:

$$\langle A\rangle(t) = \langle\Psi(t)|\,A\,|\psi(t)\rangle = \sum_{i,j} c_i^*(t)c_j(t)A_{ij} \ . \tag{3.9}$$

Finally, the evolution of $|\Psi(t)\rangle$ is described by the Schrödinger equation:

$$i\hbar\left|\dot{\Psi}(t)\right\rangle = H(t)\,|\Psi(t)\rangle \ , \tag{3.10}$$

where $H(t)$ is the Hamiltonian of the system and $\dot{\square} = d/dt$.

Description by a density operator

Equation (3.9) states that the coefficient $c_k(t)$ is included in the mean of a quadratic expression of the type $c_i^*(t)c_j(t)$. These are just the matrix elements of the operator $|\Psi(t)\rangle\langle\Psi(t)|$ projected onto the state vector as shown in Eq. (3.12):

$$\left[|\Psi(t)\rangle\langle\Psi(t)|\right]_{ij} = \langle i|\Psi(t)\rangle\,\langle\Psi(t)|j\rangle = \sum_{k,n} c_n^*(t)c_k(t)\delta_{ik}\delta_{nj} \ , \tag{3.11}$$

$$\Rightarrow\ \left[|\Psi(t)\rangle\langle\Psi(t)|\right]_{ij} = c_j^*(t)c_i(t) \ . \tag{3.12}$$

Now we define the *density operator* by

$$\rho(t) \equiv |\Psi(t)\rangle\langle\Psi(t)| \ . \tag{3.13}$$

The density operator is represented in the $\{|k\rangle\}$ basis by a matrix called the *density matrix* whose elements are

$$\rho_{ij}(t) = \langle i|\,\rho(t)\,|j\rangle = c_j^*(t)c_i(t) \ . \tag{3.14}$$

We will show that the specification of $\rho(t)$ is sufficient to characterize the quantum state of the system; that is, it allows us to obtain all physical predictions that can be computed from $|\Psi(t)\rangle$. To do this, we write the formulas (3.8), (3.9) and (3.10) in relation to $\rho(t)$:

$$\sum_k |c_k(t)|^2 = \sum_k c_k^*(t)c_k(t) = \sum_k \rho_{kk}(t) = 1 \,, \tag{3.15}$$

$$\Rightarrow \ \mathrm{Tr}\{\rho(t)\} = 1 \,. \tag{3.16}$$

Once $A_{ij} = |i\rangle A |j\rangle$ and $\rho_{ij}(t) = c_j^*(t)c_i(t)$, we have:

$$\langle A\rangle(t) = \sum_{k,n} c_k^*(t)c_n(t) \langle k| A |n\rangle = \sum_{k,n} \rho_{nk}(t) \langle k| A |n\rangle \ \ , \tag{3.17}$$

$$\Rightarrow \ \langle A\rangle(t) = \sum_{k,n} \langle n| \rho(t) |k\rangle\langle k| A |n\rangle = \sum_{n} \langle n| \rho(t)A |n\rangle \ \ , \tag{3.18}$$

$$\Rightarrow \ \langle A\rangle(t) = \mathrm{Tr}\{\rho(t)A\} = \mathrm{Tr}\{A\rho(t)\} \,. \tag{3.19}$$

Time evolution

The time evolution of the operator $\rho(t)$ can be deduced from the Schrödinger equation:

$$\begin{cases} H(t)\,|\Psi(t)\rangle = i\hbar \left|\dot{\Psi}(t)\right\rangle \\ \\ \langle\Psi(t)| = -i\hbar \left\langle\dot{\Psi}(t)\right| \end{cases} . \tag{3.20}$$

Deriving the Eq. (3.13) with respect to t, we have

$$\dot{\rho}(t) = \left|\dot{\Psi}(t)\middle\rangle\middle\langle\Psi(t)\right| + \left|\Psi(t)\middle\rangle\middle\langle\dot{\Psi}(t)\right| \ , \tag{3.21}$$

$$\Rightarrow \ [H(t), \rho(t)] = i\hbar\dot{\rho}(t) \,. \tag{3.22}$$

3.1.2 Measure probability and the statistical mixture of states (non-pure case)

Consider a_k as the measurement obtained in the measurement of an observable A and $\mathscr{P}_k(a_\ell)$ the probability of measure a_ℓ at time t. The projector onto the eigensubspace associated with the measure of a_ℓ is $\Pi_\ell \equiv |\ell\rangle\langle\ell|$ and the probability $\mathscr{P}_k(a_\ell)$ is the average of Π_ℓ [6]. Thus

$$\mathscr{P}_k(a_\ell) = \langle k| \Pi_\ell |k\rangle = \mathrm{Tr}\{\rho_k\Pi_\ell\}, \tag{3.23}$$

where $\rho_\ell = |\ell\rangle\langle\ell|$ is the density operator associated with the state $|\ell\rangle$.

Definition of the mixed density operator

Now we consider a system for which the various probabilities $p_1, p_2, \ldots, p_k, \ldots$ are arbitrary, constrained by

$$\begin{cases} 0 \leq p_k \leq 1\ ;\ k = 1, 2, 3, \ldots \\ \\ \displaystyle\sum_k p_k = 1 \end{cases} . \tag{3.24}$$

According to Eq. (3.23), we have

$$\mathscr{P}(a_\ell) = \sum_k p_k \operatorname{Tr}\{\rho_k \Pi_\ell\}\ , \tag{3.25}$$

$$\Rightarrow\ \mathscr{P}(a_\ell) = \operatorname{Tr}\left\{\sum_k p_k \rho_k \Pi_\ell\right\}\ , \tag{3.26}$$

from where we define:

$$\rho \equiv \sum_k p_k \rho_k\ . \tag{3.27}$$

A collection of pure states $|k\rangle$ with probability p_k leads to a single density operator ρ, but the converse is usually not true: the same density operator can be interpreted as several different statistical mixtures of pure states. For example, in an N-dimensional state space, a statistical mixture of N equally likely states $\{|k\rangle\}$ produces a density operator:

$$\rho = \frac{1}{N}\mathbb{1}\ , \tag{3.28}$$

where $\mathbb{1}$ is the identity operator. In other words, the density operator is an *equivalence class* [7] of indistinguishable ensembles.

3.2 First law: the energy exchange between the system and the reservoir

The mean value of energy of a quantum system is

$$\langle E\rangle = \operatorname{Tr}\{\rho(t)H(t)\}\ , \tag{3.29}$$

where $\rho(t)$ is the density operator and $H(t)$ is the hamiltonian of the system.

We are going to take the mean value of energy as the internal energy of the system, $E(t)$. Taking the differential of the expression, we end up with

$$dE(t) = \text{Tr}\{\dot{\rho}(t)H(t)\}dt + \text{Tr}\{\rho(t)\dot{H}(t)\}dt \, . \tag{3.30}$$

Defining

$$\delta W(t) \equiv \text{Tr}\{\rho(t)\dot{H}(t)\}dt \, , \tag{3.31}$$

and

$$\delta \mathscr{E}_d(t) \equiv \text{Tr}\{\dot{\rho}(t)H(t)\}dt \, , \tag{3.32}$$

we got the first law of thermodynamics for quantum systems

$$dE(t) = \delta \mathscr{E}_d(t) + \delta W(t) \, . \tag{3.33}$$

Integrating Eq. (3.33) we get the macroscopic form of the first law

$$\Delta E(t) = W(t) + \mathscr{E}_d(t) \, , \tag{3.34}$$

where

$$W(t) = \int_0^t \text{Tr}\{\rho(t')\dot{H}(t')\}dt' \tag{3.35}$$

is the work that can be invested or extracted by the system, and

$$\mathscr{E}_d(t) = \int_0^t \text{Tr}\{\dot{\rho}(t')H(t')\}dt' \tag{3.36}$$

is the energy change of the system by its interaction with the reservoir. From Eq. (3.35), we define the power of a quantum system as:

$$\mathbb{P}(t) \equiv \text{Tr}\{\rho(t)\dot{H}(t)\} \, . \tag{3.37}$$

We now define the Ergotropy of the system

$$\mathscr{W}(\rho, H) \equiv \text{Tr}\{\rho H\} - \min_U \text{Tr}\{U\rho U^\dagger H\} \geq 0 \, , \tag{3.38}$$

as the maximum amount of work that can be extracted from the ρ state by unitary transformations. In Eq. (3.38), the minimization is over all unitary transformations U. If V is the transformation that minimizes $\text{Tr}\{U\rho U^\dagger H\}$, we define a passive state $\Gamma \equiv V\rho V^\dagger$ that leads us to

$$\mathscr{W} = \text{Tr}\{\rho H\} - \text{Tr}\{\Gamma H\} \, , \tag{3.39}$$

$$\Rightarrow \mathscr{W} = \text{Tr}\{(\rho - \Gamma)H\} \; . \tag{3.40}$$

Note that $\mathscr{W} = E - \text{Tr}\{\Gamma H\}$ and, then

$$E = \text{Tr}\{\Gamma H\} + \text{Tr}\{(\rho - \Gamma)H\} \; , \tag{3.41}$$

$$\Rightarrow \; E = E_{pas} + \text{Tr}\{(\rho - \Gamma)H\} \; , \tag{3.42}$$

where $E_{pas} \equiv \text{Tr}\{\Gamma H\}$. Taking the differential of Eq. (3.41), we obtain

$$dE(t) = \text{Tr}\{\dot{\Gamma} H\}dt + \text{Tr}\{\Gamma \dot{H}\}dt + \text{Tr}\{(\dot{\rho} - \dot{\Gamma})H\}dt + \text{Tr}\{(\rho - \Gamma)\dot{H}\}dt \; , \tag{3.43}$$

where, obviously, Γ, H and ρ depends on t. From Eq. (3.31) and Eq. (3.33), we can write

$$dE(t) = \delta\mathscr{E}_d(t) + \text{Tr}\{\rho \dot{H}\}dt \; , \tag{3.44}$$

that result in

$$\delta\mathscr{E}_d(t) = \text{Tr}\{\dot{\Gamma}(t)H(t)\}dt + \text{Tr}\{(\dot{\rho}(t) - \dot{\Gamma}(t))H(t)\}dt \; , \tag{3.45}$$

$$\Rightarrow \; \mathscr{E}_d(t) = Q(t) + \Delta\mathscr{W}_d(t) \; , \tag{3.46}$$

with

$$Q(t) \equiv \int_0^t \text{Tr}\{\dot{\Gamma}(t')H(t')\}dt' \; , \tag{3.47}$$

being the energy associated with a change in the passive state and thus a change in entropy. In the same way we do in classical thermodynamics, we will refer to Eq. (3.47) as the heat of the system. Once $Q(t)$ is the dissipative change in the passive energy, the term

$$\Delta\mathscr{W}_d(t) \equiv \int_0^t \text{Tr}\{(\dot{\rho}(t') - \dot{\Gamma}(t'))H(t')\}dt' \; , \tag{3.48}$$

will be the dissipative change in the system ergotropy by its interaction with the reservoir. If we have a system in which the state is always passive, then

$$Q(t) = \mathscr{E}_d(t) \; . \tag{3.49}$$

With these definitions, we can rewrite the first law as

$$\Delta E(t) = Q(t) + \mathbb{W}(t) \; , \tag{3.50}$$

where $\mathbb{W}(t) \equiv \Delta\mathscr{W}_d(t) + W(t)$.

3.3 Quantum adiabatic evolution

Suppose that you found a state $|\varphi_k(t)\rangle$ such that

$$H(t)\,|\varphi_k(t)\rangle = E_k(t)\,|\varphi_k(t)\rangle \;, \tag{3.51}$$

we call $|\varphi_k(t)\rangle$ an *instantaneous eigenstate*. In general, the instantaneous eigenstates isn't a solution to the time dependent Schrödinger equation, but we can construct a good approximation to the solution using these eigenstates. The time dependent Schrödinger equation is

$$i\hbar\left|\dot{\Psi}(t)\right\rangle = H(t)\,|\Psi(t)\rangle \;. \tag{3.52}$$

We define the *dynamical phase* of the state as

$$\theta_k(t) \equiv -\frac{1}{\hbar}\int_0^t E_k(\xi)d\xi \;, \tag{3.53}$$

and suppose that the solution have the form

$$|\Psi(t)\rangle = c_k(t)e^{i\theta_k(t)}\,|\varphi_k(t)\rangle \;. \tag{3.54}$$

The right hand side (RHS) is

$$H(t)\,|\Psi(t)\rangle = c(t)e^{i\theta_k(t)}H(t)\,|\varphi_k(t)\rangle \;\Rightarrow\; H(t)\,|\Psi(t)\rangle = E_k(t)\,|\Psi(t)\rangle \;, \tag{3.55}$$

and the left hand side (LHS) is

$$i\hbar\frac{\partial}{\partial t}\,|\Psi(t)\rangle = i\hbar\left[\frac{d}{dt}(c_k(t)e^{i\theta_k(t)})\,|\varphi_k(t)\rangle + c_k(t)e^{i\theta_k(t)}\,|\dot{\varphi}_k(t)\rangle\right] \;, \tag{3.56}$$

$$\Rightarrow\; i\hbar\frac{\partial}{\partial t}\,|\Psi(t)\rangle = i\hbar\dot{c}_k(t)e^{i\theta_k(t)}\,|\varphi_k(t)\rangle + E_k(t)\,|\Psi(t)\rangle + i\hbar c_k(t)e^{i\theta_k(t)}\,|\dot{\varphi}_k(t)\rangle \;, \tag{3.57}$$

$$\Rightarrow\; i\hbar\frac{\partial}{\partial t}\,|\Psi(t)\rangle = i\hbar\left[\dot{c}_k(t)\,|\varphi_k(t)\rangle + c_k(t)\,|\dot{\varphi}_k(t)\rangle\right]e^{i\theta_k(t)} + E_k(t)\,|\Psi(t)\rangle \;. \tag{3.58}$$

Equating (3.55) and (3.58) results in

$$\dot{c}_k(t)\,|\varphi_k(t)\rangle + c_k(t)\,|\dot{\varphi}_k(t)\rangle = 0 \;, \tag{3.59}$$

$$\Rightarrow\; \langle\varphi_k(t)|\,\dot{c}_k(t)\,|\varphi_k(t)\rangle = -\,\langle\varphi_k(t)|\,c_k(t)\,|\dot{\varphi}_k(t)\rangle \;, \tag{3.60}$$

$$\Rightarrow\; \frac{\dot{c}_k(t)}{c_k(t)} = i\nu_k(t) \;\Rightarrow\; c_k(t) = c_k(0)e^{i\gamma_k(t)} \;, \tag{3.61}$$

where $\nu_k(t) \equiv i \langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle$ is a projection parameter and $\gamma_k(t) \equiv \int_0^t \nu_k(\xi) d\xi$ is the *Berry's geometric phase* of the state. Finally, we have

$$|\Psi(t)\rangle \approx c_k(0) e^{i\theta_k(t)} e^{i\gamma_k(t)} |\varphi_k(t)\rangle \ . \tag{3.62}$$

We have not put an equality sign in Eq. (3.62), since the time dependent Schrödinger equation is a vector equation, and the inner product $\langle \varphi_k(t) | \Psi(t) \rangle$ is a projection of $|\Psi(t)\rangle$ on the instant eigenstate and thus it is a necessary condition to solution, but not sufficient. We need to check if the solutions forms a complete basis of states. Obviously, once we know $|\varphi_k(t)\rangle$, the equation can only have a solution if the two states $|\varphi_k(t)\rangle$ and $|\dot{\varphi}_k(t)\rangle$ are in the same "direction". This doesn't happen in general and thus, we will limit this approximation to systems in which the hamiltonian changes slowly in time.

- **The Adiabatic Quantum Theorem**: consider the complete set $\{|\varphi_n(t)\rangle\}$ of orthonormal instantaneous eigenstates of the hamiltonian $H(t)$:

$$H(t) |\varphi_n(t)\rangle = E_n(t) |\varphi_n(t)\rangle \ , \tag{3.63}$$

with $E_1(t) < E_2(t) < \cdots < E_{N-1}(t) < E_N(t)$, that is, we have no degeneracies.

If we have $|\Psi(t=0)\rangle = |\varphi_n(t=0)\rangle$ for some n, then if $H(t)$ is an *adiabatic invariant* for $0 \leq t \leq \mathscr{T}$, then at time $\mathscr{T}$ we have $|\Psi(\mathscr{T})\rangle \approx |\varphi_n(\mathscr{T})\rangle$, differing by a calculable phase.

- **Further results of the adiabatic theorem**:

1. The probability of transition to another state $|\varphi_{k\neq n}(t)\rangle$ is approximately zero.
2. The phase shift between two instantaneous eigenkets can have geometrical meaning.

Now we are going to calculate the $|\Psi(t)\rangle$ for the time dependent Schrödinger equation with more precision, assuming that

$$|\Psi(t)\rangle = \sum_n c_n(t) |\varphi_n(t)\rangle \ . \tag{3.64}$$

Putting Eq. (3.64) in Eq. (3.52) we obtain

$$i\hbar \sum_n \left[\dot{c}_n(t) |\varphi_n(t)\rangle + c_n(t) |\dot{\varphi}_n(t)\rangle \right] = \sum_n c_n(t) E_n(t) |\varphi_n(t)\rangle \ . \tag{3.65}$$

Acting $\langle\varphi_k(t)|$ on the left of Eq. (3.65) we are left with

$$i\hbar\dot{c}_k(t) + i\hbar\sum_n c_n(t)\,\langle\varphi_k(t)|\dot{\varphi}_n(t)\rangle = c_k(t)E_k(t)\ , \tag{3.66}$$

$$\Rightarrow\ i\hbar\dot{c}_k(t) + i\hbar c_k(t)\,\langle\varphi_k(t)|\dot{\varphi}_k(t)\rangle + i\hbar\sum_{n\neq k} c_n(t)\,\langle\varphi_k(t)|\dot{\varphi}_n(t)\rangle = c_k(t)E_k(t)\ , \tag{3.67}$$

$$\Rightarrow\ \dot{c}_k(t) = -c_k(t)\left[\frac{i}{\hbar}E_k(t) + \langle\varphi_k(t)|\dot{\varphi}_k(t)\rangle\right] - \sum_{n\neq k} c_n(t)\,\langle\varphi_k(t)|\dot{\varphi}_n(t)\rangle\ . \tag{3.68}$$

If we differentiate the Eq. (3.63), we get

$$\dot{H}(t)\,|\varphi_n(t)\rangle + H(t)\,|\dot{\varphi}_n(t)\rangle = \dot{E}_n(t)\,|\varphi_n(t)\rangle + E_n(t)\,|\dot{\varphi}_n(t)\rangle\ . \tag{3.69}$$

Acting $\langle\varphi_k(t)|$ on the left of Eq. (3.69) considering $n \neq k$, we end up with

$$\langle\varphi_k(t)|\dot{\varphi}_n(t)\rangle = \frac{\left[\dot{H}(t)\right]_{kn}}{E_n(t) - E_k(t)}\ , \tag{3.70}$$

where $\left[\dot{H}(t)\right]_{kn} \equiv \langle\varphi_k(t)|\,\dot{H}(t)\,|\varphi_n(t)\rangle$ are the kn matrix elements of $\dot{H}(t)$ on the instantaneous eigenkets basis. Therefore, we estimate a correction factor for the adiabatic approximation. In this way, if $H(t)$ is an adiabatic invariant, then $\dot{H}(t) \approx 0$ and then

$$\dot{c}_k(t) \approx ic_k(t)\left[\nu_k(t) - \frac{E_k(t)}{\hbar}\right]\ , \tag{3.71}$$

and then

$$\ln\left(\frac{c_k(t)}{c_k(0)}\right) \approx i\left(\int_0^t \nu_k(\xi)d\xi\right) + i\left(-\frac{1}{\hbar}\int_0^t E_k(\xi)d\xi\right)\ , \tag{3.72}$$

$$\Rightarrow\ c_k(t) \approx c_k(0)e^{i\theta_k(t)}e^{i\gamma_k(t)}\ , \tag{3.73}$$

$$|\Psi(t)\rangle \approx \sum_n c_n(0)e^{i\theta_n(t)}e^{i\gamma_n(t)}\,|\varphi_n(t)\rangle\ , \tag{3.74}$$

The probability $P_s(t)$ of measure the vector $|\Psi(t)\rangle$ on the state $|\varphi_s(t)\rangle$ is

$$P_s(t) = |\langle\varphi_s(t)|\Psi(t)\rangle|^2 = |c_s(0)|^2\ \Rightarrow\ P_s(t) = P_s(0)\ , \tag{3.75}$$

that means that *the adiabatic evolution preserves the probability.*

3.4 The quantum Otto cycle

Consider that we have a system in witch the state is prepared to execute a cycle in four stages:

1. The system has the probability $1 - p_u^{(1)}(0)$ in the lower state immediately before being brought into contact with a reservoir at temperature T_1. The system is put in contact with the reservoir for a time τ_1, when it achieves a probability $p_u^{(1)}(\tau_1)$ to gain some energy from the reservoir and transition to the most energetic state, with an energy gap ε_1.
2. The system is then isolated from the thermal reservoir and undergoes a quantum adiabatic *expansion* to reduce the energy gap ε_1 to a smaller value ε_2, maintaining the probability as the adiabatic evolution theorem guarantees. Since it's an expansion, we have a quantity of work performed *by* the system.
3. The system, with probability $p_u^{(2)}(0)$ of being in the upper state is brought into contact with another reservoir at temperature T_2 for some time τ_2 until it reaches a probability $1 - p_u^{(2)}(\tau_2)$ to release some energy to the reservoir and jump down the gap ε_2 to be in the lower state.
4. The system is put out of contact with the reservoir and suffers an adiabatic *contraction*, receiving external work and increasing the energy gap ε_2 again to ε_1.

Figure 3.1 illustrates the energy levels of the quantum Otto engine. The internal energy of the system is

$$U = \langle E \rangle = \sum_i p_i E_i \ , \tag{3.76}$$

where p_i and E_i are, respectively, the probability of occupation and the energy of the i-th level. Taking the differential of the Eq. (3.76), we have

$$dU = \sum_i E_i dp_i + \sum_i p_i dE_i = \delta\mathscr{E}_d + \delta W \ . \tag{3.77}$$

Note that we do not need and do not specify temperatures for the quantum system; all temperatures are properties of the reservoir assumed to be in the Gibbs state. However, in the Otto cycle, the absorption and release of energy in the 1 and 3 phases is neither definitely nor deterministic. Quantum mechanics tells us that they can only occur probabilistically, and that the probability of this transition occurring depends on the details of the interaction with the heat bath and some intrinsic properties (namely, temperature). The cyclic nature of the heat engine limits the probability: $p_u^{(1)}(0) = p_u^{(2)}(\tau_2)$ and $p_u^{(2)}(0) = p_u^{(1)}(\tau_1)$. The net work done by our quantum heat engine in the two quantum adiabatic channels in phases 2 and 4 is, from (3.77), given $\varepsilon_1 > \varepsilon_2$,

$$\Delta W = -p_u^{(1)}(\tau_1)(\varepsilon_2 - \varepsilon_1) - p_u^{(2)}(\tau_2)(\varepsilon_1 - \varepsilon_2) \; , \tag{3.78}$$

$$\Rightarrow \; \Delta W = -(p_u^{(1)}(\tau_1) - p_u^{(2)}(\tau_2))(\varepsilon_2 - \varepsilon_1) \; , \tag{3.79}$$

since the system produces/receives work only in stages 2 and 4. The minus sign holds by our convention in Eq. (2.5). The heat transferred to the system is

$$Q_{in} = (p_u^{(2)}(\tau_2) - p_u^{(1)}(\tau_1))\varepsilon_1 \; . \tag{3.80}$$

If the system can thermalize with the reservoirs in the stages 1 and 3, we have:

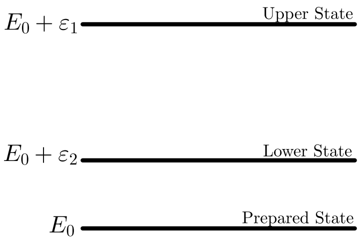

FIGURE 3.1: schematic view of the energy levels of the quantum Otto engine.

- Case (i)—stage 1: the system can occupy either the prepared state or the upper state at temperature T_1.

The partition function of the system, on the equilibrium, is

$$Z^{(1)} = e^{-\beta_1 E_0} + e^{-\beta_1 (E_0 + \varepsilon_1)} \; . \tag{3.81}$$

The equilibrium probability of finding our system on the upper state is

$$\widetilde{p}_u^{(1)} = \frac{e^{-\beta_1 (E_0 + \varepsilon_1)}}{Z^{(1)}} \; \Rightarrow \; \widetilde{p}_u^{(1)} = \frac{1}{1 + e^{\beta_1 \varepsilon_1}} \; . \tag{3.82}$$

- Case (ii)—stage 3: the system can occupy either the prepared state or the lower state at temperature T_2.

The partition function of the system, on the equilibrium, is

$$Z^{(2)} = e^{-\beta_2 E_0} + e^{-\beta_2 (E_0 + \varepsilon_2)} \; . \tag{3.83}$$

The equilibrium probability of finding our system on the upper state is

$$\widetilde{p}_u^{(2)} = \frac{e^{-\beta_2(E_0+\varepsilon_2)}}{Z^{(2)}} \Rightarrow \widetilde{p}_u^{(2)} = \frac{1}{1+e^{\beta_2\varepsilon_2}} \;, \tag{3.84}$$

and hence

$$\widetilde{p}_u^{(i)} = \frac{1}{1+e^{\beta_i\varepsilon_i}} \;,\; i = 1, 2 \;; \tag{3.85}$$

where $\beta_i \equiv 1/k_b T_i$. Putting Eq. (3.85) on Eq. (3.79), we end up with

$$W = -\frac{(\varepsilon_2 - \varepsilon_1)\left(e^{\beta_2\varepsilon_2} - e^{\beta_1\varepsilon_1}\right)}{(1+e^{\beta_1\varepsilon_2})(1+e^{\beta_2\varepsilon_2})} \;. \tag{3.86}$$

The probabilities in Eq. (3.85) are definitely nonzero. Therefore, even in the case of $T_2 \geq T_1$ there exist, even with a small probability $\widetilde{p}_u^{(1)}(1 - \widetilde{p}_u^{(2)})$, cycles in which the transitions described in stages 1 and 3 above actually take place[3]. According to the probabilistic nature of quantum mechanics, there are certain cycles whose the only result is the absorption of heat into work, of the amount $(\varepsilon_2 - \varepsilon_2)$. This amounts to a violation of the **(K)** statement of the second law of thermodynamics. This violation, however, occurs only randomly, with some small probability, and thus is not exploitable.

However, there is a safe way to *always* extract the work of $(\varepsilon_1 - \varepsilon_2)$ on each completed cycle. To remove probabilistic uncertainty, we prepare the system to be in a lower state until stage 1; we perform energy measurements after stage 1, and only let the engine continue to stage 2 if the measurement confirms that the system is in a upper state; then We take another measurement after phase 3 and let the system continue to phase 4 only if the measurement confirms that the system is in a lower state. All of this can be done even for the case of $T_2 \geq T_1$, extracting in a controlled way some works that would otherwise be prohibited by the second law. This apparent violation of the second law is simply the result of the behavior of Maxwell's demon [4].

After each cycle, the measurement apparatus, acting as Maxwell's demons, have recorded the results needed to determine the next phase of engine operation. In this way, even if we assume that the quantum measurement step itself consumes no energy and leaves no net effect anywhere else, there will be additional effects and changes in the device's registers/memory. In order to remove these residues and restore strict cyclicity, we must restore the registers to their original state, erasing all information gained in the cycle by resetting their bits or thermally treating the

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[3] The probability, however, diminishes exponentially for $\mathscr{N}$ consecutive cycles: $\left[\widetilde{p}_u^{(1)}(1 - \widetilde{p}_u^{(2)})\right]^{\mathscr{N}}$, in all of which the system performs a net work on the environment.

registers with a heat bath. In any case, the additional effect is unavoidable, i.e. each erased bit releases at least $k_b T \ln 2$ of heat (Landauer principle, [4]) and the the second law still holding. Despite the random quantum mechanical violation, the second law is upheld on the average and the work that can be performed by our engines in thermal equilibrium when, and only when, as can be seen from Eq. (3.86), $p_u^{(1)}(\tau_1) > p_u^{(2)}(\tau_2)$, and thus when and only when, from Eq. (3.85),

$$T_1 > \frac{T_2 \varepsilon_1}{\varepsilon_2} \,. \tag{3.87}$$

The expressions (3.78) and (3.87) not only confirm the broad validity of the second law but also refine the law further in specifying how much T_1 must be larger than T_2 before some work can be extracted. In other words, work cannot be extracted, on the average, even when T_1 is greater than T_2 but less than $T_2\varepsilon_2/\varepsilon_2$, in contradistinction to the classical necessary condition that T_1 needs only to be larger than T_2. Thus, the efficiency of the engine is

$$\eta = \frac{|\Delta W|}{Q_{in}} = 1 - \frac{\varepsilon_2}{\varepsilon_1} \,, \tag{3.88}$$

which is independent of the temperature of the reservoirs.

Chapter 4

Conclusions

The present work aimed to discuss the basic physical principles needed to study quantum thermodynamic cycles. It is expected that the reader has been able to understand the fundamental principles of classical thermodynamics: equilibrium, energy, reversible and irreversible processes, and, of course, the physics of ideal thermal machines, which is essential for understanding the principle of entropy increase of a isolated system. All of these concepts are essential for an introduction to quantum thermodynamics.

After studying classical thermodynamics, our work moves to quantum mechanics and, in a simple and objective way, we show how to describe an ensemble of quantum states through a density operator. This description is important, since the information of this ensemble is incomplete due to the non-determinism present in quantum mechanics. Thanks to the description of our density operator system, we hope that the reader has been able to understand what a statistical mixture of states is and, consequently, the basic principles of quantum thermodynamics: the first law and the difference between heat, work and power in the quantum and classical regimes.

Since the main objective of this work is the study of the quantum Otto cycle, it was necessary to describe what is a quantum adiabatic evolution and its main consequence: the conservation of probability. Furthermore, we were able to study the quantum Otto cycle, which is capable of producing an amount of work equivalent to the heat given to the cycle, presenting an apparent violation of the statement **(K)**, corresponding to an action of the demon of Maxwell, who plays the role of the measuring apparatus used in the system.

However, the second law of thermodynamics is ensured by the way in which we prepare and control the evolution of the system in conjunction with Landauer's principle. Finally, we have refined the second law by showing that the relation between the reservoir temperatures must be $T_1/T_2 > \varepsilon_2/\varepsilon_2$, and not just $T_1 > T_2$ (classical case); and also we derived the efficiency of this cycle.

Chapter 5

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