



We Strive For Wisdom !!

QUANTUM THERMODYNAMICS AND WORK FLUCTUATION

A SENIOR PROJECT SUBMITTED TO COLLEGE OF NATURAL AND
COMPUTATIONAL SCIENCES DEPARTMENT OF PHYSICS

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR DEGREE OF
BACHELOR OF SCIENCE IN PHYSICS

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Wolkite, Ethiopia
June 2019

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The undersigned here by certify that they have read and recommend to the department of physics for acceptance a project entitled “ **QUANTUM THERMODYNAMICS AND WORK FLUCTUATIONS** ” by **Asmamaw Tesega** in partial fulfillment of the requirements for the degree of Bachelor of Science in Physics.

Dated: June 2019

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Dedication

This senior project work is literature review of part the work entitled “Quantum thermodynamics and work fluctuations with the applications to magnetic resonance ”that done were by wellington L.Ribeiro, Gabriel T.Landi and Fernando L.Semiao in Am. J.Phys.84,948 (2016); doi:10.1119/1.4964111. Besides, all sources or materials used for this thesis have been properly and suitably acknowledged.

Acknowledgment

First of all, I would like to thank almighty God who made it possible, to begin and finish this work successfully. I would like to express my heartfelt gratitude and great appreciation to my **Advisor: Dr.Berhanu Aragie(Ph.D.)**, for his success full, valuable contributions and suggestions during the preparation of this project work. Without his encouragement and valuable discussions and remarks this work would have not been possible. I will always remember how his ideas and suggestions always work and how he could simply pick the small mistakes. Actually he was more than advisor; he was a teacher who inspired and pushed us forward. Next, I would like to express our heartfelt thanks and appreciation to my families, for their financial and moral support. I also would like to thank our teachers from whom I took time to time help in subject and other fields. Finally, I do not miss the words of thanks toward our Head of department of physics and Faculty Dean of college of natural and computational sciences for their coordinations and helps facilities, which they have provided for the completion of this project work.

Abstract

In this senior project work, we discussed the ideas of quantum thermodynamics and work fluctuations, using only basic concepts from quantum and statistical mechanics. After reviewing the concept of work as usually taught in thermodynamics and statistical mechanics, we discussed in non-equilibrium processes work as a random variable applied in quantum systems. We also discussed the distribution of work and characteristic function. We discussed also the framework of non-equilibrium processes in quantum systems together with some modern developments, such as the Jarzynski equality and its connection to the second law of thermodynamics. We hope that this senior project will serve as an introduction for a non-equilibrium system, work, as a fluctuating parameter to a new student up to date and make aware of on the recent developments in non-equilibrium thermodynamics of quantum systems.

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List of Symbols and Abbreviations

In this senior project work, we used the following Physical Symbols and Abbreviations:

- U – Internal Energy
- W – Work Performed
- Q – Heat Energy
- F – Free Energy
- S – Entropy
- G – The characteristics function
- P – The probability distribution function
- H – Hamiltonian
- T – Temperature
- Z – Partition Function
- δ – The Dirac delta function
- Δ – The change in a certain value
- λ – The work parameter
- β – The Temperature Parameter/Boltzmann factor
- $\hat{\rho}_{th}$ – The Gibbs density operator matrix
- \hat{U} – The unitary time evolution operator

- E_n and $|n\rangle$ – The Energy eigenvalues and eigenvectors respectively
- \sum – Summation
- ψ – The wave function
- t – The time required
- i.e. – That is
- JE – Jarzynski equality
- SNNPR – South Nation Nationality People Region
- Fig.– Figure
- Eq. – Equation
- Eqs. – Equations

List of Physical Constants

In this senior project work, we used the approximated values of the following Physical constants:

- $\hbar \approx 1$: Reduced Plank's constant
- $\kappa_B \approx 1$: Boltzmann's constant
- $\pi \approx 3.14$
- $i = \sqrt{-1}$

Chapter 1

Introduction

Thermodynamics is concerned only with macroscopic quantities and ignores the microscopic variables that characterize individual molecules [1, 2]. It is a general theory of macroscopic systems which provides limits on allowable physical processes involving energy transformations and relations between various measurable quantities. Macroscopic systems are a system large enough to be visible in the ordinary sense and contains macroscopic variables, such as volume, pressure, and temperature, suffice to completely characterize a system. The concept of temperature plays a central role in thermodynamics and is related to the physiological sensation of hot and cold. Because such a sensation is an unreliable measure of temperature, we will develop the concept of temperature by considering what happens when two bodies are placed so that they can exchange energy. The most important property of the temperature is its tendency to become equal. For example, if we put a hot and a cold body into thermal contact, the temperature of the hot body decreases and the temperature of the cold body increases until both bodies are at the same temperature and the two bodies are in thermal equilibrium. A macroscopic system can be described in detail by specifying its micro state. Such a description corresponds to giving all the possible information. Because thermodynamics describes the macroscopic properties of macroscopic systems without appeal to arguments based on the nature of their microscopic constituents, the concepts of energy and entropy in this context are very abstract. However, after the advent of the atomic theory, microscopic systems are constantly fluctuating due to the inherent chaos and randomness of the micro-world.

Statistical mechanics provides a microscopic foundation for thermodynamics and can be used to make quantitative predictions about macroscopic systems. The statistical mechanics is to begin with the microscopic laws of physics that govern the behavior of the constituents of the system and deduce the properties of the system as a whole. Statistical mechanics is a bridge between the microscopic and macroscopic worlds.

1.1 Statement of the problem

In this project work we would have been expected to answer the following questions:

- How the idea that work can be treated as a random variable?
- We then show that how to construct all of its statistical properties such as the corresponding probability distribution of work or the characteristic function?

1.2 Objective of the study

1.2.1 General objective

In this project work:

- We give a pedagogical introduction to the ideas of quantum thermodynamics and work fluctuations, using only basic concepts from quantum and statistical mechanics.
- To introduce the reader to the idea that work can be treated as a random variable.

1.2.2 Specific objective

- After reviewing the concept of work as usually taught in thermodynamics and statistical mechanics; we discuss in non-equilibrium processes work as a random variable applied in quantum systems.
- We also discuss the distribution of work and characteristic function.
- Based on the above information, we drive the Jarzynski equality.

1.3 Significance of the study

- To bring the readers up to date on the recent developments in non-equilibrium thermodynamics of quantum systems together with some modern developments, such as the Jarzynski equality and its connection to the second law of thermodynamics.
- This project work is a remarkable achievement of modern-day physics that we are now able to test the second law of thermodynamic is always valid on average.

1.4 Scope of the study

In this project work we use both isothermal processes in equilibrium statistical mechanics and non equilibrium unitary dynamics to study the probability distribution of work and characteristic function from quantum systems, by considering work as a random variable.

1.5 Limitation of the study

When we study this project work, we would have been the following limitations:

- Difficulty to get relevant information on the related topic.
- There is no enough book .
- Lack of internet accessibility.
- Lack of more time to do this project work.

1.6 Definitions of terms and concepts

Macro state of a system refers to its macroscopic properties, such as its temperature, pressure, volume and density.

A partition function In physics, it describes the statistical properties of a system in thermodynamics.

An intensive parameters is a physical quantity whose value does not depend on the amount of the substance for which it is measured.

An extensive parameters is a physical quantity whose value is proportional to the size of the system it describes, or to the quantity of matter in the system. It depends on the amount of substance.

An observables a dynamical variables that can be measured.

An irreversible process a process that can go only one direction.

A reversible process a process that can restore the system and its surroundings to their original condition.

Thermodynamic parameters are macroscopic variables which describe the macro state of the system.

Chapter 2

Review of Literature

In this chapter we will discuss about macroscopic systems and introduce the basic concepts of thermodynamics. We also provide a brief review of thermodynamics with particular emphasis upon the techniques for manipulating state functions needed to exploit statistical mechanics fully.

2.1 Background theory

Thermodynamics was initially developed to deal with macroscopic systems [1, 2]. If it is large enough to be visible in the ordinary sense and is thus based on the idea that a handful of macroscopic variables, such as volume, pressure, and temperature, suffice to completely characterize a system. However, after the advent of the atomic theory, it became clear that the variables of the underlying microscopic world are constantly fluctuating due to the inherent chaos and randomness of the micro-world. Statistical mechanics was thus developed as a theory connecting these microscopic fluctuations with the emergent macroscopic variables. Because one usually deals with a large number of particles, the relative fluctuations become negligible, so that thermodynamic measurements usually coincide very well with expectation values of the microscopic fluctuating quantities (a consequence of the law of large numbers)[3]. In recent years statistical mechanics has evolved into the more general field of statistical physics. Statistical physics is characterized more by its techniques than by the problems that are of interest.

Equilibrium statistical mechanics is now a well established and successful theory. Its main result is the Gibbs formula for the canonical ensemble [4–6] which provides a fundamental bridge between microscopic physics and thermodynamics for any equilibrium situation. Conversely, far less is known about non-equilibrium processes. The reason is that in this case the handful of parameters used in thermodynamics no longer suffices, forcing one to know the full dynamics of the system; i.e., one must study Newton's or Schrodinger's equations for all constituent particles, thus making the problem much more difficult.

These difficulties led researchers to look for non equilibrium processes in the realm of small systems. On the one hand, in these systems, the dynamics are somewhat easier to describe because there are fewer particles. But on the other hand, fluctuations become important and must therefore be included in the description. The random fluctuations present in small systems affect thermodynamic quantities such as work and heat. In some realizations, it is even possible to extract work without any changes in the thermodynamic state of the system something that would contradict the second law of thermodynamics. This introduces the idea that fluctuations in small systems could lead to local violations of the second law. These violations were first observed in fluid simulations in the beginning of the 1990s by Evans, Cohen, Gallavotti, and collaborators [7, 8].

Afterwards, in 1997 and 1998 came two important breakthroughs by Jarzynski [9, 10] and Crooks [11, 12]. They showed that the work performed in a non-equilibrium process, when interpreted as a random variable, obeyed a set of exact relations that touched deeply on the nature of irreversibility and the second law. The Jarzynski equality (JE) is an equation in statistical mechanics that relates free energy differences between two states and the irreversible work along an ensemble of trajectories joining the same states. It is named after the physicist Christopher Jarzynski (then at the University of Washington, currently at the University of Maryland) who derived it in 1997. In contrast to the thermodynamic statement, the Jarzynski equality remains valid no matter how fast the process happens. The contribution of Jarzynski [9, 10] was to show that by interpreting W as a random variable, one can obtain an equality, even for a process performed arbitrarily far from equilibrium. Nowadays, researchers began to look for some results in quantum systems, both for unitary [13, 14] and for open [15, 16] quantum dynamics.

Chapter 3

Methodology

This chapter aims to provide an introduction to some of the most important concepts employed when dealing with this project entitled on “Quantum thermodynamics and work fluctuations.” In particular, we review and illustrate the essential concepts, methods and principles which are going to be used in this project, while skipping rigorous demonstrations and referring to more specific books or reviews on this project. We started by reviewing the necessary concepts of thermodynamics and statistical mechanics needed for the description of work. We also focused the isothermal processes in equilibrium statistical mechanics. Next, we focused on the case of non-equilibrium unitary dynamics by interpreting work as a random variable applied in quantum systems or the dynamical evolution of closed quantum systems, and its relation with the second law of thermodynamics experienced by one of its constituents in the case of many-body systems. Finally, we focused the distribution of work and characteristic function, together with some modern developments, such as the Jarzynski equality and its connection to the second law of thermodynamics.

3.1 Research work area and period

The study had been conducted in Wolkite University which is found in Ethiopian SNNPR, Guraghe Zone, 170 km South West of Addis Ababa on the way to Jimma. Wolkite University is situated at Gubreye sub-city, 15 km away from Wolkite town of the Gubreye Butajira road. The study had been conducted from March to June 2019 for four months.

3.2 Source of data

The information for this study had been gathered in different ways. the source of information is only secondary source of data. The sources of information are literature review of part the project entitled on “Quantum thermodynamics and work fluctuations with the applications to magnetic resonance” that done were by wellington L.RibeiroGabriel

T.LandiFernando L.Semiao in Am. J.Phys. 84,948 (2016); doi:10.1119/1.4964111, and other published articles, internet, text books.

3.3 Project design

The study of this project was based on theoretical view and it was about quantum thermodynamics and work fluctuations with both in an equilibrium and a non-equilibrium processes. This study had been conducted to identify the effect of interpreting work as a random variable on a second law of thermodynamics.

Chapter 4

Mathematical Derivations

In this chapter we deal with the mathematical machinery needed to study quantum thermodynamics and work fluctuation. Although this chapter is mathematical in scope, no attempt is made to be mathematically complete. We limit ourselves to those practical issues that are relevant to the formalism of quantum thermodynamics by treating work as a random variable. For this, we will also examine the mathematics involved in representing all of its statistical properties, such as the corresponding probability distribution and the characteristic function of a system by considering work as a random variable.

4.1 Work in thermodynamics and statistical mechanics

4.1.1 Thermodynamic description

Consider any physical system described by a certain Hamiltonian. When this system is placed in contact with a heat reservoir, energy may flow between the system and the bath. This change in energy is called heat. But the energy of a system may also change by means of an external agent, which manually changes some parameter in the Hamiltonian of the system. These types of changes are called work. Hence, thermodynamics is concerned with energy and changes of energy that are distinguished as heat and work. Heat and work are not properties of the system. Rather, they are the outcomes of processes that alter the state of the system. During a certain interval of time some amount of heat Q entered the system and work W was performed on the system.

Using conservation of energy,

$$\Delta U = Q + W \tag{4.1}$$

which is the first law of thermodynamics. When $W > 0$ we say the external agent performed work on the system, while when $W < 0$ we say the system performed work on the external agent.

The process of performing work on a system can be characterized through the changing of some parameter λ in the Hamiltonian. We call it the work parameter. In order to describe how the work was performed exactly, we must specify the protocol under what conditions and with what time dependence $\lambda(t)$ does the work performed. The process lasts between a time $t = 0$ and a time $t = \tau$, during which λ varies in some predefined way from an initial value $\lambda_i = \lambda(0)$ to a final value $\lambda_f = \lambda(\tau)$. A quasi-static process is the process, that fixes intensive parameters of the system and results equilibrium. Since the system always exchanges energy with the heat bath in isothermal process. The part of U available for performing work is called the free energy F , so that

$$W = \Delta F = \Delta U - Q \quad (4.2)$$

Eq.(4.2) holding only for the isothermal (i.e. quasistatic) process. Where $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$. The energy is “free” in the sense that it is available to perform work. Now suppose we try to repeat the same process too quickly, so that it cannot be considered as quasi-static. The initial state in all cases is $F(\lambda_i)$, but not be the final state $F(\lambda_f)$. This implies that, $\Delta F \neq F(T, \lambda_f) - F(T, \lambda_i)$. However, the system is coupled to a bath, after the protocol is over, it relaxes to the state $F(\lambda_f)$. Thus, overall a certain amount of work W was performed to take the system from $F(\lambda_i)$ to $F(\lambda_f)$. But this work is not equal to ΔF . According to the second law of thermodynamics, the work done in the non-equilibrium process must always be larger than ΔF , so that in general

$$W \geq \Delta F \quad (4.3)$$

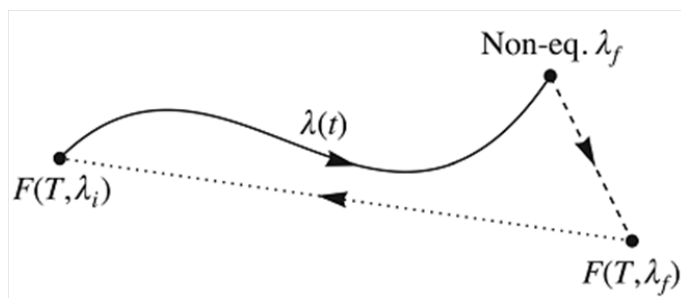


Figure 4.1: Diagram representing a non-equilibrium process. Through the protocol λ_t , the system is taken from an initial state $F(\lambda_i)$ to a final non equilibrium state with parameter λ_f (solid line). After the process is done, the system will eventually relax from the non-equilibrium state to the equilibrium state $F(\lambda_f)$ (dashed line). Finally, the dotted line represents the journey back to the original state.

Rather, ΔF is the minimum work performed when the system in an isothermal quasi-static process. Any other protocol will require more work. The difference $W_{irr} = W - \Delta F \geq 0$ known as the irreversible work. According to the second law of thermodynamics, it is impossible to extract work with a fixed temperature of a system, unless some thermodynamics states are changed. Extracting work while changing the thermodynamic state of a system is not a problem. To make the connection with Eq.(4.3), consider a process divided into three steps, represented by the three lines in Fig 4.1. In the first step, we perform a certain amount of work W in a non-equilibrium process. In the second, we perform no work and allow the system to relax from the non equilibrium state to $F(\lambda_f)$. Finally, in the third process (represented by a dotted line in Fig 4.1), we go back quasi statically from $F(\lambda_f)$ to $F(\lambda_i)$. The amount of work required for the return journey is $W_{return} = -\Delta F$, because we assume that this part is quasi-static. In the end, we are back to the original state, having performed a total work $W + W_{return} = W - \Delta F$. This total work cannot be negative, because that would mean we would have extracted work from a reservoir at a fixed temperature, without any changes in the state of the system. Consequently, in accordance with the second law of thermodynamics.

$$W - \Delta F \geq 0 \tag{4.4}$$

4.1.2 Isothermal processes in equilibrium statistical mechanics

A quasistatic transformation is one which occurs so slowly that the system is always arbitrarily close to equilibrium. Since the process is a quasi-static process, we can decompose such process into a series of infinitesimal processes, where λ changes slightly to $\lambda + d\lambda$. If initially we have a system with Hamiltonian $H(\lambda) = H$ in thermal equilibrium with a heat bath at a temperature T . According to statistical mechanics, its state is then given by the Gibbs density operator

$$\rho_{th} = \frac{e^{-\beta H}}{Z} \tag{4.5}$$

Where $Z = tr(e^{-\beta H})$ is the partition function and $\beta = \frac{1}{T}$ in units with Boltzmann's constant equal to 1 ($\kappa_B = 1$). In terms of the energy eigenvalues E_n and eigenvectors $|n\rangle$, The probability of finding the system in the state $|n\rangle$ is

$$P_n = \langle n | \rho_{th} | n \rangle = \frac{e^{-\beta E_n}}{Z} \tag{4.6}$$

Moreover, the internal (average) energy of the system can be written as

$$U = \langle H \rangle = \sum_n E_n P_n = tr(H \rho_{th}) \tag{4.7}$$

When we change λ to $\lambda + d\lambda$, both E_n and P_n will change, hence, U will change by

$$\begin{aligned} dU &= \sum_n d(E_n P_n) \\ dU &= \sum_n [d(E_n) P_n + E_n d(P_n)] \\ dU &= \sum_n d(E_n) P_n + \sum_n E_n d(P_n) \end{aligned}$$

By referring equation Eq.(4.1) we have $dU = dW + dQ$. We use δ instead of d since heat and work are not exact differentials [2]. Therefore, dU reduces to

$$dU = \delta W + \delta Q \quad (4.8)$$

is a proper differential because U is a state function even though both the heat absorbed by the system and work done on the system are improper or process-dependent differentials; i.e., both of them depends on the initial and final states and on the path. They are not a state function. From this we conclude that

$$\delta W = \sum_n (dE_n) P_n \quad (4.9)$$

$$\delta Q = \sum_n E_n (dP_n) \quad (4.10)$$

The change in λ is infinitesimal and instantaneous, so immediately after the change the system has not yet responded. This situation corresponds to the work performed in Eq. (4.9), it is the average of the energy change dE_n over the old (unperturbed) probabilities P_n . While, the energies are fixed and the probabilities change, the system adjusts itself with the bath in order to return to equilibrium. This situation corresponds to the heat exchanged in Eq.(4.10). We started with δW and show that it is related to the free energy of the system, defined as

$$F = -T \ln Z \quad (4.11)$$

Since the temperature T is fixed, so that

$$dF = -T \frac{dZ}{Z} \quad (4.12)$$

From, $Z = \sum_n e^{-\frac{E_n}{T}}$ we have $dZ = \sum_n \frac{\partial Z}{\partial E_n} dE_n = -\frac{1}{T} \sum_n e^{-\frac{E_n}{T}} dE_n$ and

$$\begin{aligned} \frac{dZ}{Z} &= \frac{-\frac{1}{T} \sum_n e^{-\frac{E_n}{T}} dE_n}{Z} \\ \frac{dZ}{Z} &= -\frac{1}{T} \left[\frac{e^{-\frac{E_0}{T}} dE_0}{Z} + \frac{e^{-\frac{E_1}{T}} dE_1}{Z} + \frac{e^{-\frac{E_2}{T}} dE_2}{Z} + \dots \frac{e^{-\frac{E_n}{T}} dE_n}{Z} \right] \\ \frac{dZ}{Z} &= -\frac{1}{T} [P_0 dE_0 + P_1 dE_1 + P_2 dE_2 + \dots P_n dE_n] = -\frac{1}{T} \sum_n P_n dE_n \end{aligned}$$

Then Eq.(4.12) reduces to

$$dF = -T \frac{dZ}{Z} = -T \left(-\frac{1}{T} \sum_n P_n dE_n \right) = \sum_n P_n dE_n \quad (4.13)$$

One can then readily show that $dF = \sum_n P_n dE_n$, which is precisely Eq.(4.9) thus,

$$dF = \delta W \quad (4.14)$$

From this result, Eq.(4.2) is recovered by integrating over the several infinitesimal steps. Next, by inverting Eq.(4.6) we get that

$$\begin{aligned} e^{-\frac{E_n}{T}} &= P_n Z \\ \ln(e^{-\frac{E_n}{T}}) &= -\frac{E_n}{T} = \ln(P_n Z) \\ E_n &= -T \ln(P_n Z) \end{aligned} \quad (4.15)$$

Since $\ln e = 1$. If we substitute Eq.(4.15) into Eq.(4.10) we have

$$\begin{aligned} \delta Q &= -\sum_n T \ln(Z P_n) dP_n \\ \delta Q &= -T \sum_n \ln(P_n) dP_n - T \sum_n \ln Z dP_n \\ \delta Q &= -T \sum_n \ln(P_n) dP_n - T \ln Z \sum_n dP_n \\ \delta Q &= -T \sum_n \ln(P_n) dP_n - T \ln Z d\left(\sum_n P_n\right) \end{aligned}$$

Since $\sum_n P_n = 1$ and $d(1) = 0$. Thus, we are left only with

$$\delta Q = -T \sum_n \ln(P_n) dP_n \quad (4.16)$$

But, now note that, by the chain rule,

$$\begin{aligned} d\left(\sum_n P_n \ln P_n\right) &= \sum_n \ln P_n (dP_n) + \sum_n P_n d(\ln P_n) \\ d\left(\sum_n P_n \ln P_n\right) &= \sum_n \ln P_n (dP_n) + \sum_n \left(\frac{P_n}{P_n}\right) (dP_n) \\ d\left(\sum_n P_n \ln P_n\right) &= \sum_n \ln P_n (dP_n) + \sum_n dP_n \\ d\left(\sum_n P_n \ln P_n\right) &= \sum_n \ln P_n (dP_n) + d\left(\sum_n P_n\right) \\ d\left(\sum_n P_n \ln P_n\right) &= \sum_n \ln P_n (dP_n) \end{aligned}$$

And the last term is also zero for the same reason as above. Hence, we conclude that

$$\delta Q = -Td\left(\sum_n P_n \ln P_n\right) \quad (4.17)$$

We see that even though δ is not a function of state, it is related to the variation of a quantity that is a function of state. From the basic principle of maximize the entropy; We define the entropy as

$$S = -\kappa_B \sum_n P_n \ln P_n = -\sum_n P_n \ln P_n, dS = d\left(-\sum_n P_n \ln P_n\right) \quad (4.18)$$

Since $\kappa_B = 1$. When we insert the right-hand side of Eq.(4.18) into Eq.(4.17), δQ is finally reduces to

$$\delta Q = TdS \quad (4.19)$$

Eq.(4.19), holds only for infinitesimal processes. For finite and irreversible processes, there may be additional contributions to the change in entropy. We therefore see that, it is possible to give microscopic definitions to thermodynamic quantities such as heat and work. Moreover, it is possible to relate them to functions of state that can be constructed from the initial density matrix ρ_{th} . While these thermodynamic quantities can be defined independently of statistical mechanics.

4.2 Work as a random variable

In quantum systems both thermal and quantum fluctuations must be taken into consideration. Quantum fluctuations are related to the fact that in order to access the amount of work performed in a system, one must measure its energy and therefore, collapse the wave function. This measurement puts the system into different states with different probabilities.

4.2.1 Non-equilibrium unitary dynamics

Here we are assuming that the coupling of the system to the heat bath is so weak that during the protocol no heat is exchanged. This situation allows us to use Schrodinger's equation to describe the dynamics of the system. Initially, the system had a Hamiltonian $H_i = H(\lambda_i)$ and was in thermal equilibrium with a bath at a temperature T . The initial state of the system is then given by the Gibbs thermal density matrix in Eq.(4.5). As a first step, we measure the energy of the system. If we let E_n^i and $|n\rangle$ denote the eigenvalues and eigenvectors of H_i , then the energy E_n^i will be obtained with probability

$$p_n = \frac{e^{-\beta E_n^i}}{Z} \quad (4.20)$$

Immediately after this measurement, we initiate the protocol, changing λ from $\lambda(0) = \lambda_i$ to $\lambda(\tau) = \lambda_f$, according to some predefined function $\lambda(t)$. Since the contact with the bath is very weak, then the state of the system evolve according to

$$|\psi(t)\rangle = \hat{U}(t)|n\rangle \quad (4.21)$$

But for a time dependent system a Hamiltonian [17] can be written as $H = i\hbar\partial_t$. Therefore, the time-evolution of a state vector $|\psi(t)\rangle$ of a system is governed by the time dependent state equation,

$$\begin{aligned} i\hbar\partial_t|\psi(t)\rangle &= H(t)|\psi(t)\rangle \\ i\hbar\partial_t\hat{U}(t)|n\rangle &= H(t)\hat{U}(t)|n\rangle \end{aligned}$$

where $\hat{U}(t)$ is the unitary time-evolution operator, which satisfies Schrodinger's equations above with ($\hbar = 1$), so that

$$i\partial_t\hat{U}(t) = H(t)\hat{U}(t), \hat{U}(0) = 1 \quad (4.22)$$

Notice that for a unitary time-evolution operator U , $\hat{U}^\dagger = \hat{U}^{-1}$ and $\hat{U}^{-1}\hat{U} = \hat{U}^\dagger\hat{U}$. At the end of the process, the Hamiltonian is now $H_f = H(\lambda_f)$, theretofore may have E_m^f and $|m\rangle$ the eigenvalues and eigenvectors of H_f , the probability that we now measure an energy E_m^f is

$$|\langle m|\psi(\tau)\rangle|^2 = |\langle m|\hat{U}(\tau)|n\rangle|^2 \quad (4.23)$$

which can be interpreted as the conditional probability that a system initially in $|n\rangle$ will be found $|m\rangle$ after a time τ . The system is completely isolated from the environment; no heat is exchanged with the it, therefore any change in the energy must be attributed to the work performed by the external agent. The energy obtained in the first measurement was E_n^i and the energy obtained in the second measurement was E_m^f . We then define the work performed by the external agent as

$$W = E_m^f - E_n^i \quad (4.24)$$

Both E_n^i and E_m^f are fluctuating quantities that change during each realization of the experiment. The first energy E_n^i is random due to thermal fluctuations, and the second energy E_m^f , is random due to quantum fluctuations. Consequently, W will also be a random variable, in accordance with both thermal and quantum fluctuations.

4.2.2 Distribution of work and characteristic function

We are dealing here a process with a two-step measurement process. From probability theory, if A and B are two events, the total probability $P(A, B)$ that both events occur can be written as

$$P(A, B) = P(A|B)P(B) \quad (4.25)$$

Where $P(B)$ is the probability that B occurs and $P(A|B)$ is the conditional probability that A occurs under the condition that B occurred. In our context, $P(A|B)$ is given by

$$P(A|B) = |\langle m|\psi(\tau)\rangle|^2 = |\langle m|\hat{U}(\tau)|n\rangle|^2 \quad (4.26)$$

Whereas $P(B)$ is simply the initial probability P_n . Hence, the probability that both events have occurred is

$$Prob(E_n^i \rightarrow protocol \rightarrow E_n^f) = |\langle m|\hat{U}(\tau)|n\rangle|^2 P_n \quad (4.27)$$

So, the probability of the work performed can be written as

$$P(W) = \sum_{n,m} |\langle m|\hat{U}(\tau)|n\rangle|^2 P_n \delta[W - (E_m^f - E_n^i)] \quad (4.28)$$

Where $\delta(x)$ is the Dirac delta function. We sum over all allowed events, weighted by their probabilities, and catalog the terms according to the values of $E_m^f - E_n^i$. Although it is exact, Eq.(4.28) is not very convenient to work with. In most systems, there are a large number of allowed energy levels and therefore an even larger number of allowed energy differences $E_m^f - E_n^i$. It is much more convenient to work with the characteristic function, defined as the Fourier transform of the original distribution

$$G(r) = \langle e^{irW} \rangle = \int_{-\infty}^{\infty} P(W) e^{irW} dW \quad (4.29)$$

From $G(r)$ we can recover the original distribution from the inverse Fourier transform

$$P(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dr G(r) e^{-irW} \quad (4.30)$$

Because, $P(W)$ and $G(r)$ are Fourier transforms of each other, they contain the same information. With the help of Eq.(4.28) we can write

$$\begin{aligned} G(r) &= \sum_{n,m} |\langle m|\hat{U}(\tau)|n\rangle|^2 P_n e^{ir(E_n^f - E_n^i)} \\ G(r) &= \sum_{n,m} \langle n|\hat{U}^\dagger(\tau) e^{irE_n^f} |m\rangle \langle m|\hat{U}(\tau) e^{-irE_n^i} P_n |n\rangle \\ G(r) &= \sum_{n,m} \langle n|\hat{U}^\dagger(\tau) e^{irH_f} |m\rangle \langle m|\hat{U}(\tau) e^{-irH_i} \rho_{th} |n\rangle \end{aligned}$$

Finally, this equation reduces to

$$G(r) = tr\{\hat{U}^\dagger(\tau) e^{irH_f} \hat{U}(\tau) e^{-irH_i} \hat{\rho}_{th}\} \quad (4.31)$$

In many aspects, the characteristic function plays a role similar to the partition function Z , uses the characteristic function as a convenient quantity from which some observable s such as the energy and entropy can be extracted.

From $G(r)$ we can also readily extract the statistical moments of W . To see this, we can expand Eq.(4.29) in a Taylor series in r to find

$$G(r) = \langle e^{irW} \rangle = 1 + ir\langle W \rangle - \frac{r^2}{2}\langle W^2 \rangle - i\frac{r^3}{3!}\langle W^3 \rangle + \dots$$

Hence, $\langle W^n \rangle$ will be multiplied by the term of order r^n in the expansion and by neglecting higher order terms this expansion reduces to

$$G(r) = 1 + ir\langle W \rangle \quad (4.32)$$

On the other hand, by doing a similar expansion in Eq.(4.31) we have

$$\begin{aligned} G(r) &= \text{tr}\{\hat{U}^\dagger(\tau)(1 + ir(H_f - H_i))\hat{U}(\tau)\hat{\rho}_{th}\} \\ G(r) &= \text{tr}\{\hat{U}^\dagger(\tau)\hat{U}(\tau)\} + ir\text{tr}\{\hat{U}^\dagger(\tau)(H_f)\hat{U}(\tau)\hat{\rho}_{th}\} - ir\text{tr}\{\hat{U}^\dagger(\tau)(H_i)\hat{U}(\tau)\hat{\rho}_{th}\} \\ G(r) &= 1 + ir\langle H_f \rangle_\tau - ir\text{tr}\{\hat{U}(\tau)\hat{U}^\dagger(\tau)(H_i)\hat{U}(0)\hat{U}^\dagger(0)\hat{\rho}_{th}\} \\ G(r) &= 1 + ir\langle H_f \rangle_\tau - ir\text{tr}\{\hat{U}^\dagger(0)(H_i)\hat{U}(0)\hat{\rho}_{th}\} \end{aligned}$$

Finally, this expansion reduces to

$$G(r) = 1 + ir\langle H_f \rangle_\tau - ir\langle H_i \rangle_0 \quad (4.33)$$

By equating these two expansions in Eq.(4.32) and Eq.(4.33) the average work, is found to be

$$\begin{aligned} 1 + ir\langle W \rangle &= 1 + ir\langle H_f \rangle_\tau - ir\langle H_i \rangle_0 \\ \langle W \rangle &= \langle H_f \rangle_\tau - \langle H_i \rangle_0 \end{aligned}$$

From this equations we see that $\langle W \rangle$ is the difference between the average energy at time τ and the average energy at time 0. Where, given any operator A , we define

$$\langle \hat{A} \rangle_t = \text{tr}\{\hat{U}^\dagger(t)A\hat{U}(t)\rho_{th}\} \quad (4.34)$$

As the expectation value of this operator at time t , a result that follows directly from the fact that the state of the system at time t is $\rho(t) = \hat{U}(t)\rho_{th}\hat{U}^\dagger(t)$.

4.2.3 The Jarzynski equality

The contribution of Jarzynski [8, 9] was to show that by considering W as a random variable, one can obtain an equality, even for a process performed arbitrarily far from equilibrium. The characteristic function can also be used to demonstrate the Jarzynski equality. Based on the definition in Eq.(4.29), if we let $r = i\beta$, we should have

$$G(r = i\beta) = \langle e^{-\beta W} \rangle \quad (4.35)$$

But, from Eqs.(4.5) and (4.31) we find that

$$\begin{aligned}
G(r) &= \text{tr}\{\hat{U}^\dagger(\tau)e^{irH_f}\hat{U}(\tau)e^{-irH_i}\rho_{th}\} \\
G(i\beta) &= \text{tr}\{\hat{U}^\dagger(\tau)e^{-\beta H_f}\hat{U}(\tau)e^{\beta H_i}\rho_{th}\} \\
G(i\beta) &= \text{tr}\{\hat{U}^\dagger(\tau)e^{-\beta H_f}\hat{U}(\tau)\frac{1}{Z_i}\} \\
G(i\beta) &= \frac{1}{Z_i}\text{tr}\{\hat{U}^\dagger(\tau)e^{-\beta H_f}\hat{U}(\tau)\} \\
G(i\beta) &= \frac{1}{Z_i}\text{tr}\{e^{-\beta H_f}\} = \frac{Z_f}{Z_i}
\end{aligned}$$

But, from Eq.(4.5) we should have $\frac{1}{Z_i} = \rho_{th}e^{\beta H_i}$ and from the fundamental properties of unitary time-evolution operator; $\text{tr}\{\hat{U}(t)^\dagger Y \hat{U}(t)\} = \text{tr}\{Y\}$, $\hat{U}(\tau)^\dagger \hat{U}(\tau) = 1$ and $\text{tr}\{XY\} = \text{tr}\{YX\}$. From $F = -T \ln Z$, we have $Z = e^{-\frac{F}{T}}$ and on the other hand, $Z = e^{-\beta E_n}$. This two relation yields the partition function as

$$Z = e^{-\frac{F}{T}} = e^{-\beta E_n} = e^{-\beta F} \quad (4.36)$$

Finally, Eq.(4.29) reduces to

$$G(i\beta) = \langle e^{-\beta W} \rangle = \frac{Z_f}{Z_i} = \frac{e^{-\beta F_f}}{e^{-\beta F_i}} = e^{-\beta \Delta F} \quad (4.37)$$

So, we conclude that the jarzynski equality holds for a process arbitrarily far from equilibrium.

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \quad (4.38)$$

where $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$ and using Jensens inequality, which states that $\langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle}$. Combining this equation with Eq.(4.38), finally we get that Clausius inequality - no free lunch on average

$$\langle W \rangle \geq \Delta F \quad (4.39)$$

As we apply thermodynamics to smaller and smaller systems the second law becomes “blurred” and statistical fluctuations about the average become important. Let $P(W)$ be the probability of performing work W , then the average work will be

$$\langle W \rangle = \int P(W)dW \quad (4.40)$$

In macroscopic systems, by the law of large numbers [3], individual measurements are usually very close to the average, so the distinction between the average work $\langle W \rangle$ and a single stochastic realization W is immaterial. But for microscopic systems, this is usually not true. In fact, although $\langle W \rangle \geq \Delta F$, the individual realizations W may very well be smaller than ΔF . These instances would be local violations of the second law. For large systems, these local violations become extremely rare. If we know the distribution $P(W)$, then the probability of a local violation of the second law can easily be found as

$$\text{Prob}(W < \Delta F) = \int_{-\infty}^{\Delta F} P(W)dW \quad (4.41)$$

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

In this study we give a pedagogical introduction to the ideas of quantum thermodynamics and work fluctuations, using only basic concepts from quantum and statistical mechanics. After reviewing the concept of work as usually taught in thermodynamics and statistical mechanics, we discuss the framework of non-equilibrium processes in quantum systems together with some modern developments, such as the Jarzynski equality and its connection to the second law of thermodynamics. It is shown in detail how to build the statistics of the work, both for a single particle and for a collection of non-interacting particles. In this study, we have made the assumption that the motion of the system is unitary. The average work of the system refers to repeating the same experiment many times each time preparing the same initial system state, bringing the system in contact with the same kind of environment and applying the same protocol. In other words, during the time evolution we have assumed that the system is not connected to a heat reservoir. This is certainly true for many systems. We then show how to construct all of its statistical properties such as the corresponding probability distribution of work or the characteristic function.

Substantial insight has been gained from these advances and their combination, and a unified language is starting to emerge. This difference in perspectives has also meant that there are ideas within quantum thermodynamics where consensus is yet to be established. One of the biggest puzzles in quantum theory today is to show how the well-studied properties of a few particles translate into a statistical theory from which new macroscopic quantum thermodynamic laws emerge. This challenge is addressed by the emerging field of quantum thermodynamics which has grown rapidly over the last decade. Apart from the academic drive to clarify fundamental processes in nature, it is expected that industrial need for miniaturization of technologies to the nano scale will benefit from understanding of quantum thermodynamic processes.

Obtaining a detailed knowledge of how quantum fluctuations compete with thermal fluctuations is essential for us to be able to adapt existing technologies to operate at ever decreasing scales, and to uncover new technologies that may harness quantum thermodynamic features. Various perspectives have emerged in quantum thermodynamics, due to the interdisciplinary nature of the field, and each contributes different insights. To close, quantum thermodynamics is a rapidly evolving research field that promises to change our understanding of the foundations of physics while enabling the discovery of novel thermodynamic techniques and applications at the nano scale. This Literature review provided an introduction to a number of current trends and perspectives in quantum thermodynamics.

5.2 Recommendation

This area of research provides an opportunity to bring the student up to speed with the current research. Thus, this research is the fountain of knowledge for the sake of knowledge and an important source of providing guidelines for solving different quantum and statistical problems. It is a sort of formal training which enables one to understand the new developments in quantum field in a better way. Quantum thermodynamics is an emerging research field aiming to extend standard thermodynamics and non-equilibrium statistical physics to ensembles of sizes well below the thermodynamic limit, in non-equilibrium situations. We have aimed to give an introduction that is as simple as possible while still being useful to students. We have presented an overview of a selection of current approaches to quantum thermodynamics pursued with various techniques and interpreted from different perspectives. Many researchers in quantum thermodynamics assume that the thermodynamic entropy is naturally extended to non-equilibrium states by the information theoretic entropy. It is a remarkable achievement of modern-day physics that we are now able to test the thermodynamic properties of systems containing only a handful of particles. But, despite being an active area of research, the basic concepts in this field can be understood using only standard quantum and statistical mechanics. The purpose of this paper is to provide an introduction to some of these concepts in the realm of quantum systems. In this regard, we would like to comment on the use of the characteristic function. It is such a useful concept that we feel every student in this area should know how to work with it. Even though the use of the characteristic function may have complicated the analysis a bit, we strongly believe that it was worth the effort. We hope that this paper will serve as a tool to bring the new student up to date on the recent developments in non-equilibrium thermodynamics of quantum systems. We believe that in the future quantum thermodynamics systems will play a particularly important role in the developments of open quantum systems in addition to current approach.

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