

# Quantum thermodynamics and work fluctuations with applications to magnetic resonance

Wellington L. Ribeiro

Universidade Federal do ABC, 09210-580 Santo André, Brazil

Gabriel T. Landi<sup>a)</sup>

Universidade Federal do ABC, 09210-580 Santo André, Brazil and Instituto de Física da Universidade de São Paulo, 05314-970 São Paulo, Brazil

Fernando L. Semião

Universidade Federal do ABC, 09210-580 Santo André, Brazil

(Received 25 December 2015; accepted 21 September 2016)

In this paper, 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. We then apply these results to the problem of magnetic resonance, where all calculations can be done exactly. 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. 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. © 2016 American Association of Physics Teachers.

[<http://dx.doi.org/10.1119/1.4964111>]

## I. INTRODUCTION

Thermodynamics was initially developed to deal with macroscopic systems<sup>1,2</sup> 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<sup>3</sup>).

Equilibrium statistical mechanics is now a well-established and successful theory. Its main result is the Gibbs formula for the canonical ensemble,<sup>4,5</sup> 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 Schrödinger's equation 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. Substantial progress in experimental methods has made it possible for the first time to experiment with small systems and has therefore contributed to this shift.

The random fluctuations present in small systems also affect thermodynamic quantities such as work and heat. A beautiful example is the use of optical tweezers to fold and unfold individual RNA molecules.<sup>6</sup> The molecules are immersed in water and therefore subject to the incessant fluctuations of Brownian motion. Thus, the amount of work required to fold a molecule will be different each time we repeat the experiment and should therefore be interpreted as a random variable. The same is true of the work that is extracted from the molecule when it is unfolded. 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 example 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.<sup>7,8</sup> Afterwards, in 1997 and 1998 came two important (and intimately related) breakthroughs by Jarzynski<sup>9,10</sup> and Crooks.<sup>11,12</sup> They showed that the work performed in a non-equilibrium (e.g., fast) 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. Nowadays, these relations go by the generic name of *fluctuation theorems* (not to be confused with the fluctuation-dissipation theorem) and can be interpreted as generalizations of the second law for fluctuating systems. These theoretical findings were later confirmed by experiments on diverse systems such as trapped Brownian particles,<sup>13,14</sup> mechanical oscillators,<sup>15</sup> and biological systems.<sup>6,16</sup>

With time, researchers began to look for similar results in quantum systems, both for unitary<sup>17,18</sup> and for open<sup>19,20</sup> quantum dynamics. Here, in addition to the thermal fluctuations, one also has intrinsically quantum fluctuations, leading to a much richer platform to work with. One may therefore ask to what extent will these quantum fluctuations affect thermodynamic quantities such as heat and work. This

research was also motivated by the remarkable progress of the past decade in the experimental control of atoms and photons, particularly in areas such as magnetic resonance, ultra-cold atoms, and quantum optics. In fact, the first experimental verifications of the fluctuation theorems for quantum systems were done only recently, using nuclear magnetic resonance<sup>21</sup> and trapped ions.<sup>22</sup>

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. Our main goal is to introduce the reader to the idea that work can be treated as a random variable. We then show how to construct all of its statistical properties such as the corresponding probability distribution of work or the characteristic function. We discuss how these quantities can be used to derive Jarzynski's equality,<sup>9,10</sup> thence serving as a quantum mechanical derivation of the second law. To illustrate these new ideas, we apply our results to the problem of magnetic resonance, an elegant textbook example that can be worked out analytically.

## II. WORK IN THERMODYNAMICS AND STATISTICAL MECHANICS

### A. Thermodynamic description

Consider any physical system described by a certain Hamiltonian  $H$ . 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*.

Heat and work are not properties of the system. Rather, they are the outcomes of processes that alter the state of the system. If during a certain interval of time an amount of heat  $Q$  entered the system and work  $W$  was performed on the system, energy conservation implies that the total energy  $U$  of the system must have changed by

$$\Delta U = Q + W, \quad (1)$$

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 (for instance, when a gas expands against a piston).

The process of performing work on a system can be described microscopically in a very general way through the change of some parameter  $\lambda$  in the Hamiltonian. We shall call this the *work parameter*. Examples include the volume of a container, an electric or magnetic field, or the stiffness of a harmonic trap. In order to describe exactly how the work was performed we must also specify the *protocol* to be used. This means specifying precisely under what conditions are the changes being made and with what time dependence  $\lambda(t)$ . We usually assume that the process lasts between a time  $t = 0$  and a time  $t = \tau$ , during which  $\lambda$  varies in some pre-defined way from an initial value  $\lambda_i = \lambda(0)$  to a final value  $\lambda_f = \lambda(\tau)$ .

Overall, describing an arbitrarily fast process can be a difficult task, because it requires detailed information about the dynamics of the system and how it is coupled to the bath.

Instead, thermodynamics usually focuses on *quasi-static* processes, in which  $\lambda$  changes very slowly in order to ensure that throughout the process the system is always in thermal equilibrium. Quasi-static processes have the advantage of being *atemporal*—we do not need to specify the function  $\lambda(t)$ , but merely its initial and final values. In this paper, our focus will be on non-equilibrium processes. But before we can get there, we must first have a solid understanding of quasi-static processes.

Perhaps the most important example of a quasi-static process is the *isothermal* process, in which the temperature of the system is kept constant throughout the protocol. Because work usually changes the temperature of an isolated system, to ensure a constant temperature the system must remain coupled to a heat reservoir kept at a constant temperature  $T$ . It is also important to note that an isothermal process must *necessarily* be quasi-static. For, if the process is not quasi-static, the temperature will not remain constant or homogeneous. In fact, intensive quantities such as temperature and pressure are defined only in thermal equilibrium, so any process where these quantities are kept fixed must be quasi-static. Thus, henceforth whenever we speak of an isothermal process, it will already be implied that it is quasi-static.

In classical mechanics, we learn that the work performed on a system can be stored as potential energy and that this potential energy can be used to extract work from the system. For a thermal system undergoing an isothermal process, this is no longer true since the system must always exchange some heat with the bath. The part of  $U$  available for performing work is called the *free energy*,  $F$ , so that

$$W = \Delta F = \Delta U - Q, \quad (2)$$

where  $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$  (cf. Ref. 1 or chapter 2 of Ref. 23). The energy is “free” in the sense that it is available to perform work.

Now suppose we try to repeat the same process, but we do so too quickly, so that it cannot be considered quasi-static. The initial state is still  $F(T, \lambda_i)$ , but the final state will not be  $F(T, \lambda_f)$ . Instead, the final state will be something complicated that depends on exactly how the process was performed (see Fig. 1). Notwithstanding, because the system is coupled to a bath, if we leave it alone after the protocol is over, it will eventually relax to the state  $F(T, \lambda_f)$ . Thus, overall, a certain amount of work  $W$  was performed to take the system from  $F(T, \lambda_i)$  to  $F(T, \lambda_f)$ . But this work is not equal to  $\Delta F$ , since Eq. (2) holds only for quasi-static processes.

Instead, according to the second law of thermodynamics, the work done in the non-equilibrium process must always be larger than  $\Delta F$ , so that in general

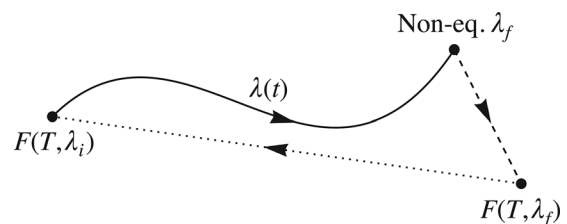


Fig. 1. Diagram representing a non-equilibrium process. Through the protocol  $\lambda(t)$ , the system is taken from an initial state  $F(T, \lambda_i)$  to a final non-equilibrium state with parameter  $\lambda_f$  (solid line). After the process is done, the system will eventually relax from the non-equilibrium state to the equilibrium state  $F(T, \lambda_f)$  (dashed line). Finally, the dotted line represents the journey back to the original state.

$$W \geq \Delta F, \quad (3)$$

with the equality holding only for the isothermal (i.e., quasi-static) process. This important result means that if we wish to change the free energy of a system by  $\Delta F$ , the *minimum* amount of work we need to perform is  $\Delta F$  and will be accomplished in an isothermal (quasi-static) process. Any other protocol will require more work. The difference  $W_{\text{irr}} = W - \Delta F \geq 0$ , known as the *irreversible work*, therefore represents the extra work that had to be done due to the particular choice of protocol.

The inequality in Eq. (3) can be interpreted as a direct consequence of the Kelvin statement of the second law: “A transformation whose only final result is to transform into work, heat extracted from a source which is at the same temperature throughout, is impossible.”<sup>1</sup> The key part of this statement is the expression “only final result.” It means that it is impossible to extract work from a bath at a fixed temperature, without changing anything else (such as the thermodynamic state of the system). Extracting work while changing the thermodynamic state of a system is not a problem. For instance, we can use a heat source to make a gas expand and thence extract work from the expansion. But by the end of the process, we will have altered the state of the gas, so the extraction of work was not the only outcome. What the second law says is that it is impossible to extract work from a single source at a fixed temperature *and* keep the state of the system intact.

To make the connection with Eq. (3), consider a process divided into three steps, represented by the three lines in Fig. 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  $F(T, \lambda_f)$ . Finally, in the third process (represented by a dotted line in Fig. 1), we go back *quasi-statically* from  $F(T, \lambda_f)$  to  $F(T, \lambda_i)$ . The amount of work required for the return journey is  $W_{\text{return}} = -\Delta F$ , because we assume that this part is quasi-static. In the end, we are back to the original state, having performed a total work  $W + W_{\text{return}} = W - \Delta F$ . According to the second law, 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,  $W - \Delta F \geq 0$ , which is Eq. (3).

## B. Isothermal processes in equilibrium statistical mechanics

Let us now analyze the isothermal process quantitatively. Because it is a quasi-static process, we can decompose it into a series of infinitesimal processes, where  $\lambda$  is changed slightly to  $\lambda + d\lambda$ . The full process is then simply a succession of these small steps.

We assume that initially we had 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

$$\rho_{\text{th}} = \frac{e^{-\beta H}}{Z}, \quad (4)$$

where  $Z = \text{tr}(e^{-\beta H})$  is the partition function and  $\beta = 1/T$  in units with Boltzmann’s constant equal to 1. We can also write this expression in terms of the energy eigenvalues  $E_n$

and eigenvectors  $|n\rangle$ . The probability of finding the system in the state  $|n\rangle$  is therefore

$$P_n = \langle n | \rho_{\text{th}} | n \rangle = \frac{e^{-\beta E_n}}{Z}. \quad (5)$$

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

$$U = \langle H \rangle = \text{tr}(H \rho_{\text{th}}) = \sum_n E_n P_n. \quad (6)$$

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

$$dU = \sum_n d(E_n P_n) = \sum_n [(dE_n)P_n + E_n(dP_n)]. \quad (7)$$

This separation of  $dU$  in two terms allows for an interesting physical interpretation.<sup>11</sup>

The change in  $\lambda$  is infinitesimal and instantaneous, so immediately after the change, the system has not yet responded. This situation corresponds to the first term on the right-hand side of Eq. (7): it is the average of the energy change  $dE_n$  over the old (unperturbed) probabilities  $P_n$ . In the second term, the energies are fixed and the probabilities change. We interpret this as the second step, where the system adjusts itself with the bath in order to return to equilibrium. Thus, each infinitesimal process can be separated into two parts. The first part is the work performed, while the second is the heat exchanged as the system relaxes to equilibrium.

This decomposition motivates us to define

$$\delta W = \sum_n (dE_n)P_n, \quad (8)$$

$$\delta Q = \sum_n E_n(dP_n), \quad (9)$$

so that Eq. (7) can be written as  $dU = \delta Q + \delta W$  (we use  $\delta$  instead of  $d$  simply to emphasize that heat and work are not exact differentials<sup>2</sup>). In order to better understand the physical meaning of these formulas, we will now explore them in more detail.

We start with  $\delta W$  and show that it is related to the free energy of the system, defined as

$$F = -T \ln Z. \quad (10)$$

To understand this relationship, first note that since the temperature  $T$  is fixed,  $dF = -T dZ/Z$ . Since  $Z = \sum_n e^{-E_n/T}$ , one can then readily show that  $dF = \sum_n (dE_n)P_n$ , which is precisely Eq. (8); thus,

$$\delta W = dF. \quad (11)$$

From this result, Eq. (2) is recovered by integrating over the several infinitesimal steps.

Next we turn to  $\delta Q$  in Eq. (9). Instead of trying to manipulate  $dP_n$ , we can use the following trick: invert Eq. (5) to write  $E_n = -T \ln(ZP_n)$ . If we substitute this relation into Eq. (9) we get two terms, one proportional to  $\ln(Z)$  and the other proportional to  $\ln(P_n)$ . The term with  $\ln(Z)$  will be

$$-T \sum_n \ln(Z) d(P_n) = -T \ln(Z) d\left(\sum_n P_n\right) = 0, \quad (12)$$

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

$$\delta Q = -T \sum_n (dP_n) \ln P_n. \quad (13)$$

But now note that, by the chain rule,

$$d\left(\sum_n P_n \ln P_n\right) = \sum_n (dP_n) \ln P_n + \sum_n \frac{P_n}{P_n} (dP_n), \quad (14)$$

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

$$\delta Q = -T d\left(\sum_n P_n \ln P_n\right). \quad (15)$$

We see that even though  $\delta Q$  is not a function of state, it is related to the variation of a quantity that is a function of state. We define the *entropy* as

$$S = -\sum_n P_n \ln P_n, \quad (16)$$

so that we finally arrive at

$$\delta Q = T dS. \quad (17)$$

This relation, we emphasize, 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  $\rho_{\text{th}}$ . While these thermodynamic quantities can be defined independently of statistical mechanics, we believe that this microscopic description helps to clarify their physical meanings.

### III. WORK AS A RANDOM VARIABLE

In 1997, Jarzynski discovered that great insight into the properties of non-equilibrium processes could be gained by treating work as a *random* variable.<sup>9,10</sup> For example, consider the process in which a movable piston is used to compress a gas contained in a cylinder. Since the molecules of the gas are moving chaotically and hitting the walls of the piston in all sorts of different ways, each time we press the piston the gas molecules will exert back on us a different force. This means that the work needed to achieve a given compression will change each time we repeat the experiment.

Of course, one may object that in most systems these fluctuations are negligibly small. But that does not stop us from interpreting  $W$  in this way. And, as we will soon see, this treatment does lead to several advantages. On the other hand, when dealing with microscopic systems this interpretation becomes essential because fluctuations become significant. A famous example is the work performed when folding RNA molecules,<sup>6,16</sup> already discussed in Sec. I.

In addition to thermal fluctuations, some microscopic systems also have a strong contribution from quantum fluctuations. These 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 [cf. Eq. (5)]. Thus, in quantum systems both thermal and quantum fluctuations must be taken into consideration.

### A. The Jarzynski equality

Usually, our knowledge of non-equilibrium processes is restricted only to inequalities such as Eq. (3). The contribution of Jarzynski<sup>9,10</sup> 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.

Consider several realizations of a non-equilibrium process, such as that described by the solid line in Fig. 1. At each realization, we always prepare the system in the same initial state. We then execute the protocol and measure the total work  $W$  performed. After repeating this process many times, we can construct the probability distribution of the work,  $P(W)$ . From this probability, any average can be computed. For instance, the average work will be

$$\langle W \rangle = \int P(W) dW, \quad (18)$$

or we can study the average of other quantities such as  $\langle W^2 \rangle$  and so on.

Jarzynski's main result was to show that the statistical average of  $e^{-\beta W}$  should satisfy<sup>9,10</sup>

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \quad (19)$$

where  $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$ , as described in Fig. 1. This result is nothing short of remarkable. It holds for a process performed *arbitrarily* far from equilibrium. And it is an *equality*, which is a much stronger statement than the inequalities we are used to in thermodynamics. The appearance of  $F(T, \lambda_f)$  in Eq. (19) is also surprising, since this is not the final state of the process; it would only be the final state if the process were quasi-static. Instead, as indicated in Fig. 1, the final state is a non-equilibrium state, which may differ substantially from  $F(T, \lambda_f)$ . The appearance of  $F(T, \lambda_f)$  therefore reflects the state that the system wants to go to, but cannot do so because the process is not sufficiently slow.

It is possible to show that the inequality in Eq. (3),  $W \geq \Delta F$ , is contained within the Jarzynski equality. This can be accomplished using Jensen's inequality (see chapter 8 of Ref. 3), which states that  $\langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle}$ . Combining this with Eq. (19) then gives

$$\langle W \rangle \geq \Delta F. \quad (20)$$

We therefore see that when we treat work as a random variable the old results from thermodynamics are recovered for the average work.

In macroscopic systems, by the law of large numbers (see, e.g., Ref. 3, chapter 8), 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  $\Delta F$ . These instances would be *local* violations of the second law. For large systems, these local violations become extremely rare. But for small systems, they can be measured experimentally.<sup>6,16,21</sup> If we know the distribution  $P(W)$ , then the probability of a local violation of the second law can easily be found as

$$\text{Prob}(W < \Delta F) = \int_{-\infty}^{\Delta F} P(W) dW. \quad (21)$$

The demonstration of the Jarzynski equality in Eq. (19) requires detailed knowledge of the dynamics of the system, i.e., if it is classical, quantum, unitary, stochastic, etc.<sup>24</sup> Below we will give a demonstration for one particular case of unitary quantum dynamics.

## B. Non-equilibrium unitary dynamics

We will now consider in detail how to describe work in a non-equilibrium process. As mentioned above, this requires detailed knowledge of the dynamics of the system and how it is coupled to the heat bath. The last part is by far the most difficult because it requires concepts from open quantum systems such as Lindblad dynamics or quantum Langevin equations.<sup>25</sup> We will therefore make an important simplification and assume that the coupling to the heat bath is so weak that during the protocol no heat is exchanged. This situation is actually encountered very often in experiments because many systems are only weakly coupled to the bath. It also simplifies considerably the description of the problem, because it allows us to use Schrödinger's equation to describe the dynamics of the system.

We shall consider the protocol described in Sec. II A. 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). 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  $P_n = e^{-\beta E_n^i}/Z$  [cf. Eq. (5)].

Immediately after this measurement, we initiate the protocol, changing  $\lambda$  from  $\lambda(0) = \lambda_i$  to  $\lambda(\tau) = \lambda_f$  according to some pre-defined function  $\lambda(t)$ . If we assume that during this process the contact with the bath is very weak, then the state of the system will evolve according to

$$|\psi(t)\rangle = U(t)|n\rangle, \quad (22)$$

where  $U(t)$  is the unitary time-evolution operator, which satisfies Schrödinger's equation (with  $\hbar = 1$ )

$$i\partial_t U = H(t)U, \quad U(0) = 1. \quad (23)$$

(For a derivation of this equation, see Ref. 26, chapter 2.)

At the end of the process, we measure the energy of the system once again. The Hamiltonian is now  $H_f = H(\lambda_f)$  and therefore may have completely different energy levels  $E_m^f$  and eigenvectors  $|m\rangle$ . The probability that we now measure an energy  $E_m^f$  is

$$|\langle m|\psi(\tau)\rangle|^2 = |\langle m|U(\tau)|n\rangle|^2, \quad (24)$$

which can be interpreted as the conditional probability that a system initially in  $|n\rangle$  will be found in  $|m\rangle$  after a time  $\tau$ .

Because no heat is exchanged with the environment, any change in the energy must necessarily 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

$$W = E_m^f - E_n^i. \quad (25)$$

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,  $E_m^f$ , is random due to quantum fluctuations. Consequently,  $W$  will also be a random variable, encompassing both thermal and quantum fluctuations.

## C. Distribution of work and characteristic function

We will now obtain an expression for the probability distribution  $P(W)$  obtained by repeating the above protocol several times. This can be accomplished by noting that we are dealing here 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

$$P(A, B) = P(A|B)P(B), \quad (26)$$

where  $P(B)$  is the probability that  $B$  occurs and  $P(A|B)$  is the conditional probability that  $A$  occurs given that  $B$  has occurred. In our context,  $P(A|B)$  is given in Eq. (24), whereas  $P(B)$  is simply the initial probability  $P_n$ . Hence, the probability that both events have occurred is

$$\text{Prob}(E_n^i \rightarrow \text{protocol} \rightarrow E_m^f) = |\langle m|U(\tau)|n\rangle|^2 P_n. \quad (27)$$

Because we are interested in the work performed, we then write

$$P(W) = \sum_{n,m} |\langle m|U(\tau)|n\rangle|^2 P_n \delta[W - (E_m^f - E_n^i)], \quad (28)$$

where  $\delta(x)$  is the Dirac delta function. This formula is perhaps best explained in words: we sum over all allowed events, weighted by their probabilities, and catalogue the terms according to the values of  $E_m^f - E_n^i$ .

Although it is exact, Eq. (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

$$G(r) = \langle e^{irW} \rangle = \int_{-\infty}^{\infty} P(W) e^{irW} dW. \quad (29)$$

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

$$P(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dr G(r) e^{-irW}. \quad (30)$$

Because  $P(W)$  and  $G(r)$  are Fourier transforms of each other, they contain the same information.

With the help of Eq. (28), we can write

$$\begin{aligned} G(r) &= \sum_{n,m} |\langle m|U|n\rangle|^2 P_n e^{ir(E_m^f - E_n^i)}, \\ &= \sum_{n,m} \langle n|U^\dagger e^{irE_m^f} |m\rangle \langle m|U e^{-irE_n^i} P_n |n\rangle, \\ &= \sum_{n,m} \langle n|U^\dagger e^{irH_f} |m\rangle \langle m|U e^{-irH_i} \rho_{\text{th}} |n\rangle \\ &= \text{tr}\{U^\dagger(\tau) e^{irH_f} U(\tau) e^{-irH_i} \rho_{\text{th}}\}, \end{aligned} \quad (31)$$

hence we conclude that

$$G = \text{tr}\{U^\dagger(\tau)e^{irH_f}U(\tau)e^{-irH_i}\rho_{\text{th}}\}. \quad (32)$$

The characteristic function does not have a particularly important physical meaning. But because it is written as the trace of a product of operators, it is usually much more convenient to work with than  $P(W)$ . In many aspects, this function plays a role somewhat similar to the partition function  $Z$  in equilibrium statistical mechanics. One usually does not dwell on the physical meaning of  $Z$ , but rather uses it as a convenient quantity from which observables 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 expand Eq. (29) in a Taylor series in  $r$  to find

$$G(r) = \langle e^{irW} \rangle = 1 + ir\langle W \rangle - \frac{r^2}{2}\langle W^2 \rangle - i\frac{r^3}{3!}\langle W^3 \rangle + \dots \quad (33)$$

Hence,  $\langle W^n \rangle$  will be multiplied by the term of order  $r^n$  in the expansion.

On the other hand, we can obtain quantum mechanical formulas for the moments by doing a similar expansion in Eq. (32). The average work, for instance, is found to be

$$\langle W \rangle = \langle H_f \rangle_\tau - \langle H_i \rangle_0, \quad (34)$$

where, given any operator  $A$ , we define

$$\langle A \rangle_t = \text{tr}\{U^\dagger(t)AU(t)\rho_{\text{th}}\} \quad (35)$$

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  $\rho(t) = U(t)\rho_{\text{th}}U^\dagger(t)$ . We therefore see that  $\langle W \rangle$  is simply the difference between the average energy at time  $\tau$  and the average energy at time 0, which is intuitive. One can continue with the expansion of Eq. (32) to obtain formulas for higher-order moments. Unfortunately, they do not acquire such a simple form.

The characteristic function can also be used to demonstrate the Jarzynski equality in Eq. (19) because, based on the definition in Eq. (29), we should have  $G(r = i\beta) = \langle e^{-\beta W} \rangle$ . But from Eqs. (4) and (32) we find that

$$G(i\beta) = \frac{1}{Z_i} \text{tr}(U^\dagger e^{-\beta H_f} U) = \frac{1}{Z_i} \text{tr}(e^{-\beta H_f}) = \frac{Z_f}{Z_i}, \quad (36)$$

and since  $Z = e^{-\beta F}$ , this yields Eq. (19)

$$G(i\beta) = \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \quad (37)$$

Notice that no assumptions have been made as to the speed of the process, so we conclude that the Jarzynski equality holds for a process arbitrarily far from equilibrium.

## IV. MAGNETIC RESONANCE

### A. Statement of the problem

We will now apply the concepts of Sec. III to a magnetic resonance experiment. The typical setup consists of a sample of non-interacting spin-1/2 particles (electrons, nucleons, etc.) placed under a strong static magnetic field  $B_0$  in the  $z$

direction. The Hamiltonian of this interaction can be described using the Pauli matrix  $\sigma_z$  as<sup>26</sup>

$$H_0 = -\frac{B_0}{2}\sigma_z. \quad (38)$$

For simplicity, we choose to measure the field in energy units. Moreover, because we are using  $\hbar = 1$ , the quantity  $B_0$  also represents the characteristic precession frequency of the spin. The eigenvalues of  $H_0$  are  $-B_0/2$  and  $B_0/2$ , corresponding to spin up and spin down, respectively.

When the spin is coupled to a heat bath at temperature  $T$ , its state will be given by the thermal density matrix  $\rho_{\text{th}}$  in Eq. (4). The Hamiltonian  $H_0$  is already diagonal in the usual  $|\pm\rangle$  basis that diagonalizes  $\sigma_z$ . Whenever this is true, the corresponding matrix exponential  $e^{-H_0/T}$  can be computed by simply exponentiating the eigenvalues

$$e^{-H_0/T} = \begin{pmatrix} e^{B_0/2T} & 0 \\ 0 & e^{-B_0/2T} \end{pmatrix}. \quad (39)$$

The partition function is the trace of this matrix,  $Z = \text{tr}(e^{-H_0/T}) = 2\cosh(B_0/2T)$ . The thermal density matrix  $\rho_{\text{th}} = e^{-H_0/T}/Z$  can then be written in a convenient way as

$$\rho_{\text{th}} = \begin{pmatrix} \frac{1}{2}(1+f) & 0 \\ 0 & \frac{1}{2}(1-f) \end{pmatrix}, \quad (40)$$

where  $f$  is the equilibrium magnetization of the system

$$f = \langle \sigma_z \rangle_{\text{th}} = \tanh\left(\frac{B_0}{T}\right), \quad (41)$$

corresponding to the paramagnetic response of a spin-1/2 particle.

The work protocol is implemented by applying a very small field of amplitude  $B_1$  rotating in the  $xy$ -plane with frequency  $\omega$ . That is, the work parameter  $\lambda$  is described here by the field  $\mathbf{B}_1 = (B_1 \sin \omega t, B_1 \cos \omega t, 0)$ . Typically,  $B_0 \sim 10$  T and  $B_1 \sim 0.01$  T, so we can always take as a good approximation that  $B_1 \ll B_0$ . The total Hamiltonian of the system now becomes

$$H(t) = -\frac{B_0}{2}\sigma_z - \frac{B_1}{2}(\sigma_x \sin \omega t + \sigma_y \cos \omega t). \quad (42)$$

The oscillating field plays the role of a perturbation, which, albeit extremely weak, may nonetheless promote transitions between the up and down spin states. The transitions will be most frequent at the resonance condition  $\omega = B_0$ , i.e., when the driving frequency  $\omega$  is the same as the natural oscillation frequency  $B_0$ .

To make progress, we must now compute the time evolution operator  $U(t)$  defined in Eq. (23). Usually, accomplishing this for a time-dependent Hamiltonian is a very complicated task. Luckily, for the particular choice of  $H$  in Eq. (42) the task turns out to be quite simple. The first step is to define a new operator  $\tilde{U}(t)$  from the relation

$$U(t) = e^{i\omega t \sigma_z/2} \tilde{U}(t). \quad (43)$$

Substituting this in Eq. (23), one finds that  $\tilde{U}$  must obey the modified Schrödinger equation

$$i\partial_t \tilde{U} = \tilde{H} \tilde{U}, \quad (44)$$

where

$$\tilde{H} = -\frac{(B_0 - \omega)}{2} \sigma_z - \frac{B_1}{2} \sigma_y. \quad (45)$$

We therefore see that  $\tilde{U}(t)$  evolves according to a time-independent Hamiltonian. Consequently, the solution of Eq. (44) is simply  $\tilde{U}(t) = e^{-i\tilde{H}t}$  and the full time evolution operator is

$$U(t) = e^{i\omega\sigma_z/2} e^{-i\tilde{H}t}. \quad (46)$$

It is important to notice that because  $\sigma_y$  and  $\sigma_z$  do not commute we cannot write  $U(t)$  as  $e^{i(\omega\sigma_z/2 - \tilde{H})t}$ .

It is also useful to have in hand an explicit formula for  $e^{-i\tilde{H}t}$ . This can be accomplished using the following trick. Let  $\mathcal{M}$  be an arbitrary matrix such that  $\mathcal{M}^2 = \mathbb{I}$  (where  $\mathbb{I}$  is the  $2 \times 2$  identity matrix). Then, if  $\alpha$  is an arbitrary constant, a direct power series expansion of  $e^{-i\alpha\mathcal{M}}$  yields

$$e^{-i\alpha\mathcal{M}} = \mathbb{I} \cos \alpha - i\mathcal{M} \sin \alpha. \quad (47)$$

We can apply this idea to our problem by writing Eq. (45) as

$$\tilde{H} = -\frac{\Omega}{2} (\sigma_z \cos \theta + \sigma_y \sin \theta), \quad (48)$$

where

$$\Omega = \sqrt{(B_0 - \omega)^2 + B_1^2}, \quad \tan \theta = \frac{B_1}{B_0 - \omega}. \quad (49)$$

Since  $\sigma_i^2 = \mathbb{I}$  it follows that  $(\sigma_z \cos \theta + \sigma_y \sin \theta)^2 = \mathbb{I}$ . Thus, Eq. (47) applies and we get

$$e^{-i\tilde{H}t} = \mathbb{I} \cos\left(\frac{\Omega t}{2}\right) + i(\sigma_z \cos \theta + \sigma_y \sin \theta) \sin\left(\frac{\Omega t}{2}\right). \quad (50)$$

Inserting this result into Eq. (46), we can finally write a closed (exact) formula for the full time evolution operator  $U(t)$ . After organizing the terms a bit, we get

$$U(t) = \begin{pmatrix} u(t) & v(t) \\ -v^*(t) & u^*(t) \end{pmatrix}, \quad (51)$$

where

$$u(t) = e^{i\omega t/2} \left[ \cos\left(\frac{\Omega t}{2}\right) + i \cos \theta \sin\left(\frac{\Omega t}{2}\right) \right], \quad (52)$$

$$v(t) = e^{i\omega t/2} \sin \theta \sin\left(\frac{\Omega t}{2}\right). \quad (53)$$

We see that, apart from a phase factor  $e^{i\omega t/2}$ , the final result depends only on  $\Omega$  and  $\theta$ , which in turn depend on  $B_0$ ,  $B_1$ , and  $\omega$  [cf. Eq. (49)].

To understand the physics behind  $u(t)$  and  $v(t)$ , suppose the system starts in the pure state  $|+\rangle$ . The probability that after a time  $t$  it will be found in state  $|-\rangle$  is  $|\langle -|U(t)|+\rangle|^2$ .

But looking at Eq. (51) we see that  $\langle -|U(t)|+\rangle = v(t)$ . Therefore,  $|v|^2$  represents the transition probability per unit time for a jump to occur. Moreover, the unitarity condition  $U^\dagger U = 1$  implies that  $|v|^2 + |u|^2 = 1$ , so  $|u|^2$  is the probability that no transition occurs.

From Eq. (53), we also see that  $v \propto \sin \theta$ , which therefore attributes a physical meaning to the angle  $\theta$  [defined in Eq. (49)] as representing the transition probability. This probability reaches a maximum precisely at resonance ( $\omega = B_0$ ), as we intuitively expect. In fact, at resonance Eqs. (52) and (53) simplify to

$$u(t) = e^{i\omega t/2} \cos\left(\frac{B_1 t}{2}\right), \quad (54)$$

$$v(t) = e^{i\omega t/2} \sin\left(\frac{B_1 t}{2}\right). \quad (55)$$

Now that we have the initial density matrix [Eq. (40)] and the time evolution operator [Eq. (51)], we can compute the evolution of any observable  $A$  we want using Eq. (35). For example, we could compute the evolution of the magnetization components  $\langle \sigma_i \rangle_t$ . All calculations are reduced to the multiplication of  $2 \times 2$  matrices; for instance, the magnetization in the  $z$ -direction will be

$$\langle \sigma_z \rangle_t = f(1 - 2|v|^2) = f(\cos^2 \theta + \sin^2 \theta \cos \Omega t), \quad (56)$$

where  $f$  is given in Eq. (41) and we used the fact that  $|u|^2 + |v|^2 = 1$ .

## B. Average work

When computing the expectation values of quantities related to the energy of the system, we can always use the unperturbed Hamiltonian  $H_0$  in Eq. (38) instead of the full Hamiltonian  $H(t)$  in Eq. (42), which is justified since  $B_1 \ll B_0$ . The energy of the system at any given time can therefore be found from Eq. (35) with  $A = H_0$

$$\langle H_0 \rangle_t = -\frac{B_0}{2} \langle \sigma_z \rangle_t = -\frac{B_0 f}{2} (1 - |v|^2). \quad (57)$$

The average work at time  $t$  is then simply the difference between the energy at time  $t$  and the energy at time 0

$$\langle W \rangle_t = f B_0 |v|^2 = f B_0 \frac{B_1^2}{\Omega^2} \sin^2\left(\frac{\Omega t}{2}\right), \quad (58)$$

where we recall that  $\Omega = \sqrt{(B_0 - \omega)^2 + B_1^2}$ . The average work therefore oscillates indefinitely with frequency  $\Omega/2$ , a consequence of the fact that the time evolution is unitary.

The amplitude multiplying the average work is proportional to the initial magnetization  $f$  and to the ratio  $B_1^2 / [(B_0 - \omega)^2 + B_1^2]$ . This ratio is a Lorentzian function; it has a sharp peak at the resonance frequency  $\omega = B_0$ , which becomes sharper with smaller values of  $B_1$ . The maximum possible work therefore occurs at resonance and has the value  $f B_0$ .

The equilibrium free energy, Eq. (10), is  $F = -T \ln Z$ , where  $Z = 2 \cosh(B_0/2T)$ . Thus, the free energy of the initial state (at time  $t=0$ ) and the final state (at any arbitrary time  $t$ ) are the same, giving  $\Delta F = 0$ . This is a consequence of the

fact that  $B_1 \ll B_0$ . According to Eq. (20), we should then expect  $\langle W \rangle \geq 0$ , which is indeed observed in Eq. (58).

### C. Characteristic function and distribution of work

Next we turn to the characteristic function  $G(r)$  given in Eq. (32), with both  $H_i$  and  $H_f$  replaced by  $H_0$  in Eq. (38). After carrying out the matrix multiplications, we get the following very simple formula:

$$G(r) = |u(t)|^2 + |v(t)|^2 \left[ \frac{(1+f)}{2} e^{iB_0 r} + \frac{(1-f)}{2} e^{-iB_0 r} \right]. \quad (59)$$

If we set  $r = i\beta$  and recall the definition of  $f$  in Eq. (41), we find that the term inside the square brackets becomes 1. Thus, we are left with  $\langle e^{-\beta W} \rangle = G(i\beta) = |u|^2 + |v|^2 = 1$ , which is the Jarzynski equality, Eq. (37), since  $\Delta F = 0$ .

Expanding  $G(r)$  in a power series, as in Eq. (33), we also obtain the statistical moments of the work. The first-order term will give  $\langle W \rangle$  exactly as in Eq. (58). Similarly, the second moment can be found to be  $\langle W^2 \rangle = B_0^2 |v|^2$ . As a consequence, the variance of the work is

$$\text{var}(W) = \langle W^2 \rangle - \langle W \rangle^2 = B_0^2 |v|^2 (1 - f^2 |v|^2). \quad (60)$$

Finally, we can compute the full distribution of work  $P(W)$ . The simplest way to do so is through the characteristic function. Recall from Eq. (30) that  $P(W)$  is the inverse Fourier transform of  $G(r)$ . To carry out the computation, we must use the integral representation for the Dirac delta function

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(a-b)r} dr = \delta(a-b). \quad (61)$$

Using this in Eq. (59), we then find

$$P(W) = |u|^2 \delta(W) + |v|^2 \frac{1+f}{2} \delta(W - B_0) + |v|^2 \frac{1-f}{2} \delta(W + B_0). \quad (62)$$

We therefore see that the work, interpreted as a random variable, can take on three distinct values:  $W = 0, +B_0$ , or  $-B_0$ .

The physics behind this result is the following. Looking back at the original Hamiltonian in Eq. (38), we see that  $B_0$  is the energy spacing between the up and down states. The event where  $W = +B_0$  corresponds to the situation where the spin was originally up and then flipped down (“up-down flip”). The change in energy in this case is  $B_0/2 - (-B_0/2) = B_0$ . Similarly,  $W = -B_0$  corresponds to a down-up flip. And, finally,  $W = 0$  corresponds to no flip at all.

We can also find the distribution  $P(W)$  “by hand,” using Eq. (28). For instance, the value  $W = +B_0$  corresponds to the up-down flip. The initial probability to have a particle up is  $(1+f)/2$  and the transition rate is  $|\langle -|U(t)|+\rangle|^2 = |v|^2$ . Thus,  $P(W = B_0) = |v|^2 (1+f)/2$ , which agrees with Eq. (62). The other two probabilities can be computed in an identical way.

From the second law, we expect that  $W > 0$ . But our results show that in a down-up flip we should have  $W = -B_0$ . Hence,  $P(W = -B_0)$  is the probability of observing a local

violation of the second law. On the other hand, notice in Eq. (62) that  $P(W = \pm B_0)$  is proportional to  $1 \pm f$ , where  $f = \tanh(\beta B_0)$ . Thus, up-down flips are always more likely than down-up flips, ensuring that  $\langle W \rangle \geq 0$ . That is to say, violations to the second law are always the exception, never the rule.

It is also possible to express Eq. (62) in terms only of the magnetization  $\langle \sigma_z \rangle_t$  [Eq. (56)]. This is interesting because  $\langle \sigma_z \rangle_t$  is a quantity that can be directly accessed experimentally. Substituting  $|v|^2 = (f - \langle \sigma_z \rangle_t)/2f$  in Eq. (62) gives

$$\text{Prob}(W = \pm B_0) = \left( \frac{f - \langle \sigma_z \rangle_t}{2f} \right) \frac{1 \pm f}{2}. \quad (63)$$

This formula shows that by measuring the average magnetization of a system, which is a macroscopic observable, we can extract the full distribution of work for a single spin-1/2 particle. The Jarzynski equality for a quantum system was first confirmed experimentally in Ref. 21 using magnetic resonance. However, in their experiment, it was necessary to use two interacting spins, which turns out to be a consequence of the fact that in their case  $[H_i, H_f] \neq 0$ . In our case, since  $B_1 \ll B_0$ , the initial and final Hamiltonians commute and thus we are able to relate the distribution of work to the properties of a single spin.

### D. Statistics of the work performed on a large number of particles

So far we have studied the work performed by an external magnetic field on a single spin-1/2 particle. It is a remarkable fact that with recent advances in experimental techniques, it is now possible to experiment with just a single particle. Notwithstanding, in most situations, one is still usually faced with a system containing a large number of particles. The next natural step is therefore to consider the work performed on  $N$  spin-1/2 particles. For simplicity, we will assume that the particles do not interact (otherwise the problem would be much more difficult).

The work corresponds to energy differences and for non-interacting systems, energy is an additive quantity. Hence, the total work  $\mathcal{W}$  performed during a certain process will be the sum of the work performed on each individual particle

$$\mathcal{W} = W_1 + \dots + W_N. \quad (64)$$

Because all spins are independent, it follows from this result that  $\langle \mathcal{W} \rangle = N \langle W \rangle$ , where  $\langle W \rangle$  is the average work in Eq. (58); this is a manifestation of the fact that work, as with energy, is an extensive quantity.

The problem has thus been reduced to the sum of independent and identically distributed random variables, something that is discussed extensively in introductory probability courses (e.g., Ref. 3, chapter 6). It is in problems such as this that the characteristic function shows its true power. Because the variables are statistically independent, we have from Eq. (64) that

$$\langle e^{ir\mathcal{W}} \rangle = \langle e^{ir(W_1 + \dots + W_N)} \rangle = \langle e^{irW_1} \rangle \dots \langle e^{irW_N} \rangle. \quad (65)$$

Moreover, since all spins are identical each term on the right-hand side corresponds exactly to the characteristic function  $G(r)$  in Eq. (59). Thus, the characteristic function of the total work  $\mathcal{W}$  will be



$$\mathcal{G}(r) = \langle e^{ir\mathcal{W}} \rangle = G(r)^N. \quad (66)$$

Referring back to Eq. (59), let us introduce momentarily the notation  $b_0 = |u|^2$  and  $b_{\pm} = |v|^2(1 \pm f)/2$ . Then Eq. (66) can be written as

$$\mathcal{G}(r) = (b_0 + b_+ e^{iB_0 r} + b_- e^{-iB_0 r})^N. \quad (67)$$

The importance of this formula lies in its connection with the probability distribution  $P(\mathcal{W})$ , established via the inverse Fourier transform in Eq. (30). If we expand the product in Eq. (67), we will get

$$\mathcal{G}(r) = \sum_{k=-N}^N \Gamma_k e^{irB_0 k}, \quad (68)$$

where the factors  $\Gamma_k$  are complicated combinations of the  $b$  coefficients that result from expanding Eq. (67). When we take the inverse Fourier transform, this is mapped into

$$P(\mathcal{W}) = \sum_{k=-N}^N \Gamma_k \delta(\mathcal{W} - B_0 k). \quad (69)$$

We therefore see that  $\mathcal{W}$  can take on values between  $-NB_0$  and  $NB_0$ . A work of  $NB_0$ , for instance, corresponds to an event where all spins have flipped from up to down. Similarly, a work of  $(N-1)B_0$  corresponds to  $N-1$  spins flipping. And there are  $N$  possibilities for which one of the spins did not flip. For other values the situation becomes even more complicated.

The characteristic function in Eq. (67) can also be interpreted as a random walk with  $N$  steps. In a single step, one can think of  $b_+$  and  $b_-$  as the probabilities of taking a step to the right or to the left (while  $b_0$  is the probability of not moving). If we repeat this  $N$  times, we get a characteristic function of the form (67). Moreover,  $P(\mathcal{W})$  plays the role of the distribution of discrete positions of the random walk.

Equation (69) is illustrated in Fig. 2 for an arbitrary choice of parameters, as explained in the figure caption. The important point to be drawn from this analysis is that there is a certain finite probability to observe a *negative* work  $\mathcal{W}$ . Since  $\Delta F = 0$ , these instances would then correspond to local violations of the second law. However, notice also that as the size  $N$  increases, the relative probability that  $\mathcal{W} < 0$  diminishes quickly. In fact, a more detailed analysis shows that

$$\text{Prob}(\mathcal{W} < \Delta F) \sim e^{-N}. \quad (70)$$

Thus, if the sample is macroscopic, it becomes extremely unlikely to observe such a violation. This is why, in our everyday experience, the second law is always satisfied.

Lastly, we should mention that when  $N$  is large we can approximate  $P(\mathcal{W})$  by a Gaussian distribution, as a consequence of the central limit theorem.<sup>3</sup> This distribution will have mean  $\langle \mathcal{W} \rangle = N\langle W \rangle$  and variance  $\text{var}(\mathcal{W}) = N\text{var}(W)$ , which are quantities we already know from Eqs. (58) and (60). This distribution is plotted as a solid line in Fig. 2(d), to be compared with the exact solution.

## V. CONCLUSIONS

The goal of this paper is to introduce the student to the concepts of quantum thermodynamics and work fluctuations.

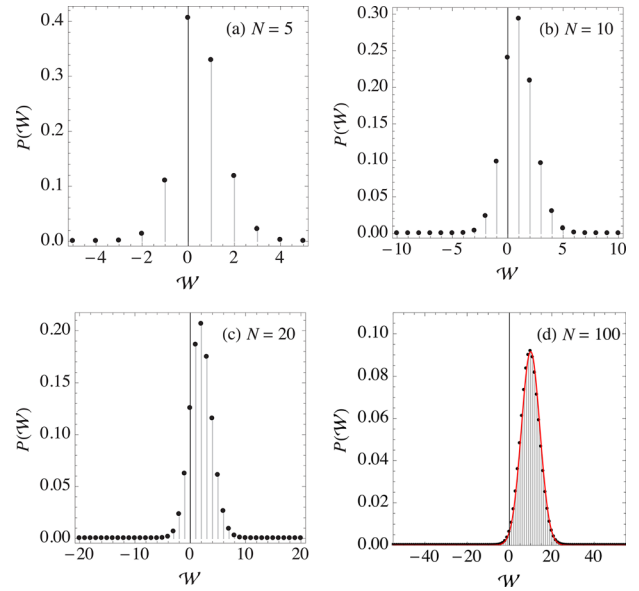


Fig. 2. The distribution  $P(\mathcal{W})$  computed from Eq. (69) for different system sizes  $N$ . The parameters used in this plot were  $B_0 = 1$ ,  $\omega = 0.8$ ,  $B_1 = 0.1$ ,  $f = 0.5$ , and  $t = \pi/\Omega$ . The solid line in panel (d) is a Gaussian distribution with the same mean and variance.

This area of research is very active and lies at the boundary between many well established areas, such as non-equilibrium statistical mechanics, quantum physics, and condensed matter; it also has deep connections with quantum information and quantum computing. Notwithstanding, unlike most frontier areas, the basic ideas can be understood using only concepts learned in standard quantum and statistical mechanics courses, thus providing an opportunity to bring the student up to speed with the current research.

We have aimed to give an introduction that is as simple as possible while still being useful to students. In this regard, we would like to comment on the use of the characteristic function. This is a concept that is not necessary, *per se*, to understand the main ideas in this paper. But 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.

In this paper, we have made the assumption that the motion of the system is unitary. 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, including nuclear magnetic resonance experiments. However, in many other scenarios, it becomes important to consider *open* quantum systems, that is, systems whose dynamics evolve coupled to a heat bath. The tools for working with open quantum systems are already extensively used in many areas, but the subject is still in its infancy. We believe that in the future these systems will play a particularly important role in the developments of this area.

## ACKNOWLEDGMENTS

The authors would like to thank Professor Mário José de Oliveira, Professor Ivan Santos Oliveira, and Professor André Timpanaro for fruitful discussions. For their financial support, the authors would like to acknowledge the Brazilian

funding agencies FAPESP (2014/01218-2) and CNPq (307774/2014-7). Support from the INCT of Quantum Information is also acknowledged.

- <sup>a)</sup>Electronic mail: gtlandi@gmail.com
- <sup>1</sup>Enrico Fermi, *Thermodynamics* (Dover, Mineola, NY, 1956).
- <sup>2</sup>Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (Wiley, New York, 1985).
- <sup>3</sup>Sheldon Ross, *A First Course in Probability*, 8th ed. (Pearson, Upper Saddle River, NJ, 2010).
- <sup>4</sup>Josiah W. Gibbs, *Elementary Principles of Statistical Mechanics*, reprinted ed. (Dover, Mineola, NY, 2014).
- <sup>5</sup>Richard P. Feynman, *Statistical Mechanics: A Set of Lectures*, 2nd ed. (Westview Press, Boulder, CO, 1998).
- <sup>6</sup>J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, and C. Bustamante, "Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality," *Science* **296**, 1832–1835 (2002).
- <sup>7</sup>D. J. Evans, E. G. D. Cohen, and G. P. Morriss, "Probability of second law violations in shearing steady states," *Phys. Rev. Lett.* **71**, 2401–2404 (1993).
- <sup>8</sup>G. Gallavotti and E. G. D. Cohen, "Dynamical ensembles in nonequilibrium statistical mechanics," *Phys. Rev. Lett.* **74**, 2694–2697 (1995).
- <sup>9</sup>C. Jarzynski, "Nonequilibrium equality for free energy differences," *Phys. Rev. Lett.* **78**, 2690–2693 (1997).
- <sup>10</sup>C. Jarzynski, "Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach," *Phys. Rev. E* **56**, 5018–5035 (1997).
- <sup>11</sup>G. E. Crooks, "Nonequilibrium measurements of free energy differences for microscopically reversible Markovian systems," *J. Stat. Phys.* **90**, 1481–1487 (1998).
- <sup>12</sup>G. E. Crooks, "Path-ensemble averages in systems driven far from equilibrium," *Phys. Rev. E* **61**, 2361–2366 (2000).
- <sup>13</sup>I. A. Martínez, É. Roldán, L. Dinis, D. Petrov, and R. A. Rica, "Adiabatic processes realized with a trapped Brownian particle," *Phys. Rev. Lett.* **114**, 120601 (2015).
- <sup>14</sup>J. R. Gomez-Solano, A. Petrosyan, and S. Ciliberto, "Heat fluctuations in a nonequilibrium bath," *Phys. Rev. Lett.* **106**, 200602 (2011).
- <sup>15</sup>F. Douarche, S. Ciliberto, A. Petrosyan, and I. Rabbiosi, "An experimental test of the Jarzynski equality in a mechanical experiment," *Europhys. Lett.* **70**, 593–599 (2005).
- <sup>16</sup>D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, and C. Bustamante, "Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies," *Nature* **437**, 231–234 (2005).
- <sup>17</sup>S. Mukamel, "Quantum extension of the Jarzynski relation: analogy with stochastic dephasing," *Phys. Rev. Lett.* **90**, 170604 (2003).
- <sup>18</sup>P. Talkner, E. Lutz, and P. Hänggi, "Fluctuation theorems: Work is not an observable," *Phys. Rev. E* **75**, 050102 (2007).
- <sup>19</sup>G. E. Crooks, "On the Jarzynski relation for dissipative quantum dynamics," *J. Stat. Mech.* **2008**, P10023.
- <sup>20</sup>P. Talkner, M. Campisi, and P. Hänggi, "Fluctuation theorems in driven open quantum systems," *J. Stat. Mech.* **2009**, P02025.
- <sup>21</sup>T. B. Batalhão, A. M. Souza, L. Mazzola, R. Auccaise, R. S. Sarthour, I. S. Oliveira, J. Goold, G. De Chiara, M. Paternostro, and R. M. Serra, "Experimental reconstruction of work distribution and study of fluctuation relations in a closed quantum system," *Phys. Rev. Lett.* **113**, 140601 (2014).
- <sup>22</sup>S. An, J.-N. Zhang, M. Um, D. Lv, Y. Lu, J. Zhang, Z.-Q. Yin, H. T. Quan, and K. Kim, "Experimental test of the quantum Jarzynski equality with a trapped-ion system," *Nat. Phys.* **11**, 193–199 (2014).
- <sup>23</sup>E. Schrödinger, *Statistical Thermodynamics* (Dover, Mineola, NY, 1989).
- <sup>24</sup>For completeness, we mention that it is very easy to demonstrate Eq. (19) in the case of infinitesimal processes as discussed in Sec. II B. But it is important to clarify that this case is physically of no interest at all: The importance of the Jarzynski equality is that it holds for non-equilibrium processes. For infinitesimal processes, we do not need such an equality. In any case, the demonstration is as follows. Based on Eq. (8), we can define the random work performed in an infinitesimal process as  $\delta W = dE_n = E_n(\lambda + d\lambda) - E_n(\lambda)$ . Equation (8) can then be interpreted instead as the definition of  $\langle \delta W \rangle$ . In other words,  $P_n$  is the probability distribution of the random variable  $\delta W$ . We can then compute any type of average we want. In particular,  $\langle e^{-\beta \delta W} \rangle = \sum_n e^{-\beta \delta W} P_n = \sum_n e^{-\beta \delta W} (e^{-\beta E_n(\lambda)} / Z(\lambda)) = \frac{1}{Z(\lambda)} \sum_n e^{-\beta E_n(\lambda + d\lambda)} = ((Z(\lambda + d\lambda)) / (Z(\lambda))) = e^{-\beta dF}$ , where we have used the fact that  $Z(\lambda + d\lambda) = e^{-\beta F(\lambda + d\lambda)}$ .
- <sup>25</sup>H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford U.P., New York, 2007).
- <sup>26</sup>J. J. Sakurai and J. J. Napolitano, *Modern Quantum Mechanics*, 2nd ed. (Addison-Wesley, Boston, 2010).



**Two Hydrostatic Balances**

This pair of hydrostatic balances recently came into the Greenslade Collection. They are used in the laboratory to determine the specific gravity of liquids. A plummet of known volume is hung by a fine wire from the right-hand end of the projecting arm, and the system is balanced by hanging small weights from the bosses on the arm; these usually have an interesting horse-shoe shape. A beaker containing the liquid is then slipped under the right-hand side until the plummet is completely immersed. Masses are then adjusted until the system balances once more. Subtraction gives the mass of the liquid displaced by the plummet, and the specific gravity obtained. These date from the first half of the 20th century. (Picture and Notes by Thomas B. Greenslade, Jr., Kenyon College)