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Non-Monotonic Behavior of the Thermodynamic Work as a Function of Switching Time

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Abstract It is usually believed that the second law necessarily implies the following statement: the faster we drive a system, the larger is the energetic cost for such manipulation. In the present paper, we show that this is not always the case. The energy necessary to drive a system is quantified by the thermodynamic work performed by the external observer. We have shown that there exists a regime in which this quantity reveals a non-monotonic decay as a function of the switching time. Although this effect can be more pronounced in thermally isolated systems, we claim that it can also be present under isothermal conditions. We illustrate our findings with a spin-1/2 in the presence of a time-dependent magnetic field.

Keywords Nonequilibrium thermodynamics · Irreversible processes · Second law of thermodynamics

1 Introduction

The second law of thermodynamics tells us about fundamental limits on manipulations of thermodynamic systems [9]. It imposes, for instance, a lower bound on the energy necessary for driving a system from one equilibrium state to another while it is kept in contact with a heat bath. Accordingly, such energetic cost, quantified by the thermodynamic work W performed by an external observer, has to be always greater or equal to the Helmholtz free energy difference ΔF between the two equilibrium states. This minimum value can be achieved if the driving is carried out quasistatically, i.e., if the process is performed extremely slowly. Therefore, it seems reasonable to expect W to be slightly bigger than ΔF if the driving speed is slightly bigger than zero. However, the second law does not necessarily imply that the faster we drive, the larger is the energetic cost. In other words, one should not expect in general a monotonic increase of W as the switching time decreases.

We wonder whether there is any generic feature in the behavior of W as a function of the switching time τ. This is in principle a very hard problem to solve because, for finite τ, the thermodynamic work depends strongly on the process we perform and on the nonequilibrium dynamics of the system of interest. To be more precise, for a finite-time process, W is a functional of the protocol we have chosen to manipulate the system, i.e., not only the initial and final values matter but also how the externally controlled parameter is varied between these two end points. Another related and interesting question is: what is the minimum energetic cost for manipulating a system given τ and the initial and final values of the externally controlled parameter? The answer to this question would establish the finite-time analog of the lower bound predicted by the second law. Although this problem of optimization in finite time dates back to the proposal of the *thermodynamic length* [4, 19, 20, 26], it has received renewed attention recently due to the interest of optimizing the manipulation of small thermodynamic systems [1, 7, 11, 12, 21, 22].

It is clear from the previous discussion that the search for generic features on the nonequilibrium behavior of W is intimately related to the physics of optimal processes in finite time. The main theoretical tools that have been used in this field are stochastic thermodynamics [5, 21, 23] and linear response theory [1, 7, 11, 22]. In the present paper,

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we briefly review and illustrate what has been achieved so far using the latter approach. In Section 2, we show that, once we are restricted to close-to-equilibrium processes, it is possible to express W as a functional of the finite-time process. They can be grouped in two distinct regimes which are briefly discussed in Sections 3 and 4. In Section 5, we illustrate one of those regimes using a spin-1/2 particle in the presence of a time-dependent magnetic field as the thermodynamic system of interest. We summarize and conclude in Section 6.

2 Finite-Time Behavior of W for Close-to-Equilibrium Processes

Our goal is to investigate the behavior of the thermodynamic work W as a function of the switching time τ. For that, our first step is to specify under which thermodynamic constraints we want to study such behavior. We shall focus here on two relevant situations: isothermal and adiabatic (in the thermodynamic sense) processes. By isothermal we mean a manipulation of the system while it is kept in contact with a heat bath. The adiabatic constraint refers to a situation in which the system is being manipulated while it is thermally isolated from the rest of the universe.

Linear response theory describes very well close-to-equilibrium processes [16, 17] and it demands that we specify the underlying microscopic dynamics for each of the thermodynamic conditions just described. For the isothermal setup, we can simply say that the Hamiltonian H_I of the system plus heat bath is composed of two parts,

$$H_I(\lambda(t)) = H_s(\lambda(t)) + H_h \,. \tag{1}$$

The first part, $H_s(\lambda(t))$, describes the time-dependent microscopic dynamics of the system of interest due to the switching of the control parameter λ, and the second one, H_h, takes into account both the coupling and the heat bath dynamics. There are very well-established ways of modeling the term H_h once the relevant information about the relaxation dynamics of the system of interest is known [7, 8]. For the adiabatic setup, we just need

$$H_A(\lambda(t)) = H_s(\lambda(t)) \,, \tag{2}$$

because the heat bath is absent.

We assume that the initial state (or probability distribution, if the system is classical) of the system described either by H_I or H_A is always a Boltzmann-Gibbs one, i.e.,

$$\rho_{eq}(\lambda) = \exp\left(-\beta H_k(\lambda)\right)/Z(\beta,\lambda) \tag{3}$$

stands for the initial density matrix or phase-space probability distribution, with $\beta = (k_B T)^{-1}$, $Z(\beta,\lambda) = \mathrm{Tr}\, e^{-\beta H_k(\lambda)}$ is the partition function and $k = I, A$ specifies the thermodynamic constraint. As mentioned before, we denote by λ the externally controlled parameter as, for instance, volume, magnetic field, etc. Work is performed on the system if λ is changed according to a predefined protocol, $\lambda(t)$, starting at t_o and ending at $t_f = \tau + t_o$. It is convenient to write

$$\lambda(t) \equiv \lambda_o + \delta\lambda\, g(t) \,, \tag{4}$$

where $g(t)$ obeys $g(t_o) = 0$ and $g(t_f) = 1$. Thus, λ is varied from $\lambda(t_0) = \lambda_o$ to $\lambda(t_f) = \lambda_o + \delta\lambda$ during the time interval $\tau \equiv t_f - t_0$. The work performed in the quasistatic limit, i.e., for $\tau \to \infty$, does not have in principle the same value for different thermodynamic conditions. For the isothermal setup, the second law predicts that $W = \Delta F$ in this limit, where

$$\Delta F \equiv F(\beta, \lambda_o + \delta\lambda) - F(\beta, \lambda_o) \,, \tag{5}$$

is given in terms of $F(\beta,\lambda) = -1/\beta \ln Z(\beta,\lambda)$. For the adiabatic setup, the thermodynamic work goes to [2, 3]

$$W_{qs} \equiv \langle E_f\rangle_o - \langle E_o\rangle_o \,, \tag{6}$$

where we denote by $\langle\cdot\rangle_o$ an equilibrium average value taken with respect to (3) for $\lambda = \lambda_o$. The quasistatic value W_{qs} is obtained from the difference between the final, $\langle E_f\rangle_o$, and initial, $\langle E_o\rangle_o$, average energies. In the classical regime, the final energy E_f is entirely determined by the initial energy E_o and the initial and final values of λ, as predicted by the mechanical adiabatic invariant [1, 13]. In the quantum regime, the mechanical adiabatic theorem [18] determines the transition probabilities between initial and final energy levels and is the relevant tool for the calculation of the final average energy value.

The behavior of W for finite-time processes can be better characterized by the following quantities: the irreversible work [24],

$$W_{irr} \equiv W - \Delta F \,, \tag{7}$$

for isothermal processes, and the excess work [1, 22],

$$W_{ex} \equiv W - W_{qs} \,, \tag{8}$$

for adiabatic ones. Since both W_{irr} and W_{ex} are zero in the quasistatic limit, they quantify the extra amount of energy provided by the external agent while carrying out a finite-time process. We adopt here the *inclusive* picture [14] to calculate W,

$$W = \int_{t_0}^{t_f} dt\, \overline{\frac{dH_k}{dt}} = \int_{t_0}^{t_f} dt\, \frac{d\lambda}{dt}\overline{\frac{\partial H_k}{\partial\lambda}} \,, \tag{9}$$

where again $k = I, A$ and $\overline{X}$ denotes the nonequilibrium average of the observable X.

Linear response theory now comes into play providing an expression for $\overline{\partial H_k/\partial\lambda}$. However, we must distinguish two regimes in which expression (9) can be used. First, the regime of slowly-varying processes [7, 11, 22] in which $\delta\lambda/\lambda_o$ can be greater than one but the ratio between the relaxation time, τ^R, of the system and the switching time τ

is much greater than one. The other regime comprises fast processes where $\delta\lambda/\lambda_o$ is much smaller than one but τ can be comparable to τ^R [1]. In what follows, we shall discuss the behavior of W predicted by linear response for each of these regimes.

3 Slowly-Varying Processes: $\tau^R/\tau \ll 1$

The regime of slowly-varying processes has been discussed exclusively for isothermal processes due to the its relevance for free energy estimation and its connection to the adiabatic switching method [11, 25]. For such thermodynamic conditions, the nonequilibrium behavior of W is characterized by the irreversible work, W_{irr}, whose expression reads

$$W_{irr} = \frac{\beta}{\tau}(\delta\lambda)^2 \int_0^1 ds \left(\frac{dg}{ds}\right)^2 \tau^c[g(s)]\mathcal{X}[g(s)]\,, \tag{10}$$

where $s \equiv (t - t_0)/\tau$.

The term $\tau^c[g(s)]\mathcal{X}[g(s)]$ is one of the elements of the more general *friction tensor* [15, 22], the quantity one has to deal with when the control parameter λ is a vector. We denote by $\tau^c[g(s)]$ the functional dependence of the *correlation* time (to be defined next) on the chosen protocol $g(s)$. Since $\lambda(t) = \lambda_o + \delta\lambda\, g(t)$, the quantity

$$\mathcal{X}[g(s)] = \left\langle (\partial_\lambda H_k)^2 \right\rangle_{g(s)} - \langle \partial_\lambda H_k \rangle^2_{g(s)}\,, \tag{11}$$

measures how the equilibrium fluctuations of the driving force, $\partial_\lambda H_k \equiv \partial H_k/\partial\lambda$, change according to the protocol $g(s)$.

The correlation time τ^c, for a fixed value of λ, is given by

$$\tau^c(\lambda) \equiv \int_0^\infty dt\, \frac{\Psi_\lambda(t)}{\Psi_\lambda(0)}\,, \tag{12}$$

where $\Psi_\lambda(t)$ stands for the *relaxation function* [16, 17], which is related via $\phi_\lambda(t) = -\dot{\Psi}_\lambda(t)$ to the *response function*,

$$\phi_\lambda(t) = \langle (\partial_\lambda H_k(0), \partial_\lambda H_k(t)) \rangle_\lambda\,. \tag{13}$$

The symbol (A, B) denotes either the Poisson bracket, $\{A, B\} = \partial_q A \cdot \partial_p B - \partial_p A \cdot \partial_q B$, for classical systems or $1/i\hbar$ times the commutator, $[A, B] = AB - BA$, for quantum systems.

Equation (10) agrees with the common intuition that claims the faster we drive, the bigger the energetic cost is. This expression predicts that the power spent along any process increases with the speed squared and W_{irr} decreases monotonically as the switching time increases. Indeed, the prefactor in (10) contains all the τ-dependence of W_{irr} and what is left can be understood as a simple geometrical factor whose minimum value is known as the thermodynamic length [20, 22]. See, for example, [7] for a detailed explanation about how such minimum can be found.

Although (10) has been derived for isothermal processes, it is also valid for adiabatic conditions as long as the integral in (12) converges. In other words, the necessary condition for the excess work to be expressed by (10) is that the relaxation function of the thermally isolated system decays sufficiently fast. Since it is not guaranteed that such decay always exists, (10) does not describe the regime of slowly-varying processes for all sorts of thermally isolated systems. Nevertheless, the adiabatic conditions require anyway two modifications of (10): first, all the equilibrium average values entering that expression have to be re-obtained considering the Hamiltonian H_A instead of H_I; second, the time-dependent observables entering (13) must be solutions of the equations of motion for Hamiltonian H_A. Fortunately, one does not need to solve the quite often impossible problem of finding such solutions. Phenomenological considerations have been proven extremely useful to capture the relevant physical behavior of $\phi_\lambda(t)$ [7, 16, 17].

4 Fast but Weak Processes: $\delta\lambda/\lambda_o \ll 1$

The expression for W_{ex} in this regime has been derived for thermally isolated systems in [1]. As mentioned before, it comprises those processes in which $\delta\lambda/\lambda_o$ is necessarily small but τ can be comparable to the relaxation time τ^R. The expression for the excess work reads

$$W_{ex} = \frac{(\delta\lambda)^2}{2} \int_0^1 ds \int_0^1 ds'\, \dot{g}(s)\, \Psi_o(\tau(s - s'))\, \dot{g}(s')\,, \tag{14}$$

where $\dot{g}(s)$ and $\dot{g}(s')$ denote the derivatives with respect to $s \equiv (t - t_0)/\tau$ and $s' \equiv (t' - t_0)/\tau$ respectively. In contrast to the previous regime, the relaxation function Ψ_o is not a functional of the protocol $\lambda(t)$. It is obtained for a fixed λ: the initial value λ_o.

The behavior of W_{ex} as a function of τ is much more involved in this case. It depends not only on the functional form of the speed but also on its convolution with the relaxation function Ψ_o. In fact, (14) is a much more complex quadratic form of the speeds than (10). Thus, it is again unadvised to claim that faster processes necessarily demand more energy. It has been shown recently that there are thermally isolated systems for which this is not the case [1, 10]. In the next section, we illustrate this effect with another example.

Equation (14) has another important difference compared to (10). It does not demand a sufficiently fast decay of the relaxation function. It remains valid even when the relaxation function does not decay at all, as shown in [1]. Hence, (14) describes both small and large thermodynamic systems undergoing either isothermal or adiabatic processes. The information about the thermodynamic constraints comes through the relaxation function, as mentioned

before: average values and time-dependent observables have to be obtained according to the appropriate Hamiltonian.

5 Example: Fast Driving of a Spin-1/2

To illustrate the physics for (14), we will study the finite-time behavior of the thermodynamic work performed on a spin-1/2 driven by a time-dependent magnetic field. The Hamiltonian of this systems reads

$$H_A(t) = -\frac{\hbar\gamma}{2}\vec{\sigma}\cdot\vec{B}(t)\,, \tag{15}$$

where the subscript A refers to adiabatic conditions, $\vec{\sigma}$ denotes the Pauli matrices and $\vec{B}(t)$ stands for the time-dependent magnetic field.

We will restrict ourselves to those processes that preserve the norm of $\vec{B}$, i.e., we will only consider finite-time rotations of the magnetic field. Using spherical coordinates, we have then

$$\vec{B}(t) = (B_o\sin[\varphi(t)]\cos[\theta(t)],\, B_o\sin[\varphi(t)]\sin[\theta(t)],\\ B_o\cos[\varphi(t)])\,. \tag{16}$$

Hence, the set of allowed processes is easily parametrized by the angles $\varphi(t)$ and $\theta(t)$, whose time dependence, in analogy with (4), are more conveniently expressed as

$$\varphi(t) = \varphi_o + \delta\varphi\, g_\varphi(t)\,, \tag{17}$$

and

$$\theta(t) = \theta_o + \delta\theta\, g_\theta(t)\,, \tag{18}$$

with the boundary conditions $g_{\varphi,\theta}(t_o) = 0$ and $g_{\varphi,\theta}(t_f) = 1$.

As described before, adiabatic processes are performed once the spin is thermally isolated and prepared in the state (3) as a result of its equilibration with a heat bath at constant field $\vec{B}(t_o^-) = \vec{B}_o$. Therefore, the initial angles φ_o and θ_o can be both set equal to zero without loss of generality.

Linear response theory provides a good description of W_{ex} as long as $\delta\varphi$ and $\delta\theta$ are kept sufficiently small. In this regime, one can easily show that the thermodynamic work (9) reads

$$W = \int_{t_o}^{t_f} dt\,\frac{d\varphi}{dt}\,\overline{\frac{\partial H_A}{\partial\varphi}}(t)\,, \tag{19}$$

with H_A given by (15). Hence, the angle $\theta(t)$ plays no role in the linear response regime. Following [1], it is straightforward to show that the relaxation function entering (14) is given, in this case, by the response function

$$\phi_{\varphi\varphi}(t) = \left\langle\left(\partial_\varphi H_A(0),\,\partial_\varphi H_A(t)\right)\right\rangle_{\varphi_o,\theta_o}\\ = \frac{\hbar}{2}(\gamma B_o)^2\tanh\left(\frac{\beta\hbar\gamma B_o}{2}\right)\sin(\gamma B_o t)\,. \tag{20}$$

Using $\phi_{\varphi\varphi}(t) = -\dot{\Psi}_o(t)$, we obtain the following expression for the relaxation function

$$\Psi_o(t) = \frac{\hbar\omega_o}{2}\tanh\left(\frac{\beta\hbar\omega_o}{2}\right)\cos(\omega_o t)\,, \tag{21}$$

where we have defined $\omega_o \equiv \gamma B_o$. The previous expression is an oscillatory function, meaning that this system never relaxes back to equilibrium by itself. Although this behavior might sound inappropriate for a thermodynamic system, we will see next that it leads to results compatible with standard thermodynamic requirements. Working out the linear response expression for (19) using (21), one obtains

$$W = \frac{(\delta\varphi)^2}{2}\frac{\hbar\omega_o}{2}\tanh\left(\frac{\beta\hbar\omega_o}{2}\right)\int_0^1 ds\int_0^1 ds'\,\dot{g}_\varphi(s)\\ \times\cos\left[\omega_o\tau(s-s')\right]\dot{g}_\varphi(s')\,, \tag{22}$$

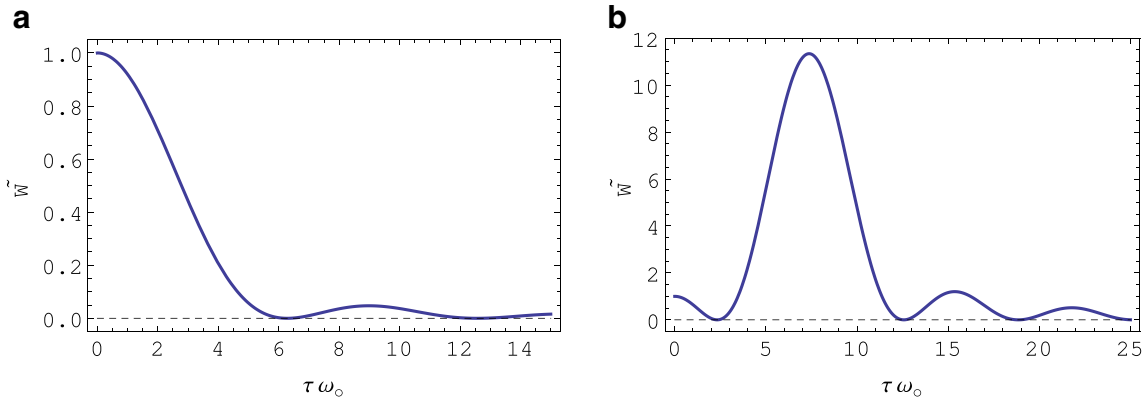

Fig. 1 Thermodynamic work as a function of the switching time τ for **a** linear, $g_\varphi(t) = (t-t_o)/\tau$, and **b** nonlinear, $g_\varphi(t) = (t-t_o)/\tau + \sin(2\pi(t-t_o)/\tau)$, protocol. The symbol $\tilde{W}$ stands for the thermodynamic work W divided by the pre-factor, $((\delta\varphi)^2/2)(\hbar\omega_o/2)\tanh(\beta\hbar\omega_o/2)$, of (22)

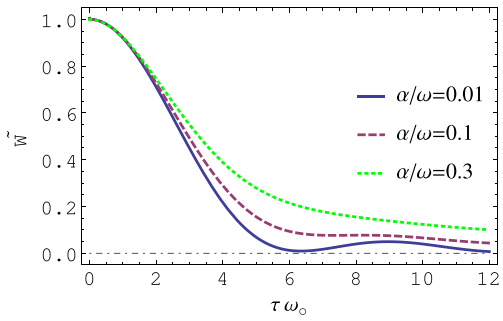

Fig. 2 Thermodynamic work as a function of the switching time for the relaxation function (23) and the linear protocol $g_\varphi(t) = (t - t_o)/\tau$. As the ratio α/ω increases, the qualitative behavior of W changes from a non-monotonic to a monotonic behavior. The symbol $\tilde{W}$ stands for the thermodynamic work W divided by the pre-factor, $((\delta\varphi)^2/2)(\hbar\omega_o/2)\tanh(\beta\hbar\omega_o/2)$, of (22)

i.e., $W = W_{ex}$ because W_{qs} is zero. This result agrees with the quantum adiabatic theorem that predicts a null quasistatic work along those processes in which the norm of $\vec{B}(t)$ is preserved.

Figure 1 shows the behavior of W given by (22) for two types of protocols. Besides the finite-time zeros of W, meaning that no energy is spent if one drives the system during specific switching times, a very pronounced non-monotonic behavior shows up as τ varies. In Fig. 1b for instance, there is a specific value of τ for which W is one order of magnitude higher than the infinitely fast driving for $\tau \to 0$. However, the thermodynamic work indeed decays to zero in both cases as τ goes to infinity, in agreement with what one expects to happen in the quasistatic limit.

6 Discussion and Conclusions

The non-monotonic behavior just discussed above is also present when the system of interest is a thermally isolated harmonic oscillator with time-dependent spring constant [1]. In fact, such feature of W is not restricted to small systems or to adiabatic conditions for (14) neither assumes specific thermodynamic constraints nor requires a small number of degrees of freedom. As discussed in [1], the relaxation function must be sufficiently oscillatory in order to produce such behavior. For instance, one can verify that for the following phenomenological ansatz [7],

$$\Psi_o(t) = \Psi_o(0)\, e^{-\alpha|t|}\left(\cos(\omega t) + \frac{\alpha}{\omega}\sin(\omega|t|)\right), \qquad (23)$$

Equation (22) leads to a non-monotonic behavior if α/ω is small enough. Moreover, Fig. 2 shows a crossover from non-monotonic to monotonic behavior as the ratio α/ω increases. Considering that the Fluctuation-Dissipation theorem relates $\Psi_o(t)$ to equilibrium time-correlations of the driving force, the non-monotonic behavior of W should show up whenever these time-correlations are weakly damped. To give a concrete example where this might happen, the phenomenological expression (23) is quite often used to describe the relaxation dynamics of weakly interacting magnetic moments modeled by the Bloch equations [6, 27].

In summary, we briefly discussed two regimes where one can find generic features on the finite-time behavior of the thermodynamic work. We showed that, for weak but fast close-to-equilibrium processes, the energetic cost of manipulating the system of interest not necessarily increases as the switching time decreases. We could relate this effect to the behavior of the equilibrium time-correlations of the system using linear response theory. We conclude that whenever such correlations survive long enough, the thermodynamic work will show a non-monotonic behavior no matter the size of the system or if it is all the time interacting with a heat bath. We believe that quantum systems at low temperatures are good candidates to observe such effects.

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