Work fluctuations due to partial thermalizations in two-level systems

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We study work extraction processes mediated by finite-time interactions with an ambient bath—*partial thermalizations*—as continuous-time Markov processes for two-level systems. Such a stochastic process results in fluctuations in the amount of work that can be extracted and is characterized by the rate at which the system parameters are driven in addition to the rate of thermalization with the bath. We analyze the distribution of work for the case in which the energy gap of a two-level system is driven at a constant rate. We derive analytic expressions for average work and a lower bound for the variance of work showing that such processes cannot be fluctuation-free in general. We also observe that an upper bound for the Monte Carlo estimate of the variance of work can be obtained using Jarzynski's fluctuation-dissipation relation for systems initially in equilibrium. Finally, we analyze work extraction cycles by modifying the Carnot cycle, incorporating processes involving partial thermalizations, and we obtain efficiency at maximum power for such finite-time work extraction cycles under different sets of constraints.

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I. INTRODUCTION

A standard thermodynamic setting is comprised of large systems with relatively short relaxation times wherein fluctuations in values of extensive quantities such as *work*, that follow the law of large numbers, are negligible and one only cares about averages [1,2]. Work is essentially a deterministic quantity in such scenarios. Nonequilibrium thermodynamics, on the other hand, is the study of *fluctuations* in work as one departs from the standard thermodynamic setting. Small systems with long relaxation times make the study of fluctuations inevitable since these are no longer just statistical noise. Within the framework of nonequilibrium statistical mechanics, fluctuations have been characterized using *fluctuation theorems* [3,4] that play a key role in the control and study of biomolecular processes such as the folding of proteins [5]. In fact, single molecule experiments involving stretching of biomolecules under external forces are a ripe avenue for the study of nonequilibrium phenomena [6–9].

A complementary approach to nonequilibrium thermodynamics is the incipient field of one-shot statistical mechanics [10–14], which draws techniques from one-shot information theory [15–18] to characterize processes that are far from equilibrium. And, within this nonequilibrium framework, work is analyzed as a random variable. In the one-shot regime one considers single instances of the task at hand instead of looking at ensemble averages. Fluctuations in work have been studied in this regime in Ref. [11] for a discrete classical model. The main question in consideration was what constituted truly worklike work extraction. The basic idea was that in order to define work for small systems in contrast to *heat*, one should be able to extract a fixed amount of work from a fixed system configuration. The author showed that for a system that is initially not in equilibrium with the ambient bath, even the optimal process (that achieves maximum average work output) results in fluctuations as large as the average work itself. Such an optimal process is comprised of (a) energy level transformations (quenches) rendering the system effectively thermal, and (b) *reversible isothermal* processes [11]. The latter is manifestly fluctuation-free because the system equilibrates at each infinitesimal step of a reversible process, and equilibration washes away the fluctuations. Of course this is only possible since the timescale over which one performs the energy level transformations (during the isothermal process) is much larger than the relaxation time of the system. The question is what happens to these fluctuations when the system only *partially* thermalizes, i.e., when the system is driven externally over shorter time periods in comparison to its relaxation timescale.

The relaxation toward equilibrium can be studied within the framework of *collision models*, which have been used to study open quantum system dynamics [19–21]. Within these models, the bath is treated as a composition of smaller noninteracting particles that are copies of the system in the thermal Gibbs state. Such a process of thermalization has been studied in Ref. [20] for a qubit in contact with a bath composed of noninteracting qubits. For a qubit in a general quantum state interacting with an ambient bath, thermalization was shown to be a two-component process comprised of decoherence and dissipation. And, a functional dependence on time was obtained for both of these processes. In the present work, we are interested in fluctuations in processes involving

partial thermalizations for classical two-level systems, and we will limit ourselves to states that are diagonal in the energy eigenbasis. With this we come to the question we posed earlier regarding fluctuations in work for processes involving partial thermalizations.

While work along these lines has been done in Ref. [22] in the low-dissipation regime (where the system is driven for large but finite time), a more closely related numerical study on this question was undertaken in Ref. [23], where the authors studied a single Ising spin driven by an external magnetic field. They obtained work distributions using Monte Carlo simulations of the processes for different driving rates. The authors found that such processes have broad work distributions with significant probability for processes with negative dissipated work in general. They also verified work fluctuation theorems [3,4] and derived analytic expressions for the distribution of work when the spin's energy gap was driven by the external field in the slow and fast limits. Another recent work [24] looked into the same problem but again in the low-dissipation regime. We will discuss this further in Sec. II.

In this paper, we investigate similar work extraction processes involving partial thermalizations for a single classical two-level system driven by an external magnetic field changing linearly in time. We derive an analytic expression for the average work yield of such a process as a function of the total time, τ. This expression reduces to the average work outputs of the corresponding adiabatic and isothermal processes in the $\tau \to 0$ and $\tau \to \infty$ limits, respectively. Next, in an attempt to characterize fluctuations in the average work yield, we provide a lower bound for the variance of work as a function of the total time duration of the process. This lower bound is saturated in the adiabatic and the isothermal limits, thereby reproducing the result that isothermal processes are deterministic, as was shown in Ref. [11]. Even though an analytical expression for the variance of work seems intractable, we employ Jarzynski's fluctuation-dissipation relation [3] to compare the dissipation in work ($\tau < \infty$) with our estimate of variance obtained by performing Monte Carlo simulations. We find that for a two-level system initially in equilibrium with the bath, the fluctuation-dissipation relation provides a good approximation that becomes exact as τ becomes large, as was also noted in Ref. [23]. Finally, we investigate finite-time work extraction cycles inspired by the Carnot cycle, replacing the ideal isothermal reversible processes with the realistic ones involving partial thermalizations. We then numerically optimize the power output of such finite-time work extraction cycles over different sets of constraints and parameters, keeping the time period of the cycles fixed, and we provide comparisons between those scenarios.

This paper is divided into six sections. In Sec. II we define finite-time work extraction processes involving partial thermalizations as a Markov process, and we describe the microscopic model for a two-level system. In Sec. III we derive the analytical results, and in Sec. IV we discuss the results from Monte Carlo simulations. We then analyze finite-time heat engines in Sec. V, and we summarize our work in Sec. VI.

II. MODEL

Given an ambient bath at temperature T_h and a two-level system such that its energy gap δ can only be driven within a fixed range between $\delta_{\min}$ and $\delta_{\max}$ (for example by an external magnetic field), let us assume that the time period of the external driving is much shorter compared to the relaxation time of the system interacting with the bath, and that the spectral density of the bath is constant over the given range of values for δ. Without loss of generality, let us further assume that the ground-state energy is zero. For a two-level system with an energy gap δ, one can always define a temperature such that the occupation probability of the excited state is given by the corresponding Gibbs distribution at that temperature. We choose time as the independent quantity under these settings, and we denote it by the continuous variable t. This brings us to the question of how one could extract work under these settings. To this end, we study finite-time work extraction processes involving *partial thermalizations*. Partial thermalization encapsulates a finite-time restriction for the system's equilibration with the bath, and it can be studied by considering a randomized model of interaction between the two—a collision model [19–21]. Such models are based on the assumption that the bath is composed of smaller noninteracting particles that are copies of the system in the thermal Gibbs state. The system-bath interaction is then modeled as a sequence of collisions between the system and bath particles where each collision itself is considered to be a joint unitary on the system and the bath particle in question. The additional assumptions of the bath being initially uncorrelated and the system colliding with exactly one bath particle at a time result in a Markovian dynamics for the system, which in turn can be translated to a Lindblad master equation in the continuous-time limit [19,25]. The process of partial thermalization was studied in Ref. [20] within the framework of a collision model, and it was shown to be composed of dissipation and decoherence for a general quantum state. For states that are diagonal in the energy eigenbasis, thermalization simply amounts to dissipation, and the state of a two-level system can be described by the occupation probabilities $p(t)$ for the excited state and $1 - p(t)$ for the ground state. Denoting the thermal Gibbs occupation probability for the excited state by $\gamma(t)$, the thermalization process is given by the following equation as per Ref. [20]:

$$p(t) = e^{-\kappa t} p(0) + (1 - e^{-\kappa t})\gamma(t), \tag{1}$$

where κ is the thermalization rate (dissipation), the inverse of the relaxation time T_1 [20]. One can interpret $1 - e^{-\kappa t}$ as the probability of collision between the qubit and a bath particle, denoting it by λ. The case $\lambda = 1$ corresponds to exact thermalization, and $\lambda = 0$ corresponds to no thermalization. Thus, for sufficiently short interaction times Δt, the probability λ with which the system interacts with the bath particles (and thermalizes) is linear in Δt, i.e., $\lambda = \kappa \Delta t$. Microscopically, partial thermalization is a time-dependent Markov process on a finite state space—the ground and excited states of our two-level system. The system with energy gap $\delta(t)$ at time t interacts with the bath for a time Δt, and with probability $\kappa \Delta t$ it collides with a bath particle. If the system thermalizes, then it can change its state such that the occupation probability for

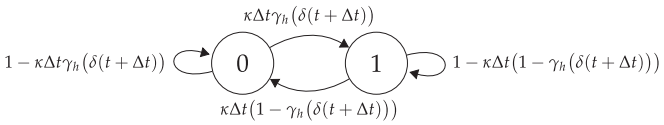


FIG. 1. Markov chain representing partial thermalization during a finite-time work extraction process when the energy gap changes from $\delta(t)$ to $\delta(t+\Delta t)$. The states 0 and 1 denote the ground and excited states of the two-level system, respectively. Each arrow is labeled by the corresponding transition probability.

the excited state is $\gamma_h(\delta(t+\Delta t))$, the thermal Gibbs weight associated with the excited state $\delta(t+\Delta t)$ for the bath temperature T_h. Work is done when the system is in the excited state and its energy gap is changed from $\delta(t)$ to $\delta(t+\Delta t)$.

We can thus build a finite-time work extraction process that involves a series of infinitesimal level transformations and partial thermalizations, along the lines of Ref. [11]. A discrete version of such a process at a given time t is, therefore, composed of a series of two steps:

(i) Level transformation: changing the energy gap $\delta(t)$ by an infinitesimal amount to $\delta(t+\Delta t)$ keeping the occupation probabilities fixed.

(ii) Partial thermalization: changing the state of the system such that with probability $1-\kappa\Delta t$ it stays in the same state, while with probability $\kappa\Delta t$ it thermalizes with respect to the bath.

The above defines a time-dependent Markov process and corresponds to the following Markov diagram:

A continuous version of the above can then be simply obtained as per the following lemma.

Lemma 1. Given a two-level system undergoing partial thermalization with a hot bath at temperature T_h (characterized by short system-bath interaction times), the occupation probability p for its excited state evolves according to the following equation:

$$\frac{dp(t)}{dt} = \kappa(\gamma_h(\delta(t)) - p(t)), \tag{2}$$

where $\gamma_h(\delta(t)) = \frac{1}{1+e^{\delta(t)/T_h}}$, the Gibbs weight associated with the instantaneous excited-state energy $\delta(t)$.

Proof. According to Fig. 1, the total probability of being in the excited state $p(t+\Delta t)$ at time step $t+\Delta t$ can be obtained using the law of total probability:

$$\begin{aligned} p(t+\Delta t) = {} & p_{01}(t+\Delta t)(1-p(t)) \\ & + p_{11}(t+\Delta t)p(t), \end{aligned} \tag{3}$$

where $p_{01}(t+\Delta t)$ is the conditional probability for the system to be in the excited state at time $t+\Delta t$ when it was in the ground state at time t, and $p_{11}(t+\Delta t)$ is the conditional probability for the system to be in the excited state at time $t+\Delta t$ when it was in the excited state at time t. Plugging in the corresponding expressions using Fig. 1, we have

$$p(t+\Delta t) = (1-\kappa\Delta t)p(t) + \kappa\Delta t\gamma_h(\delta(t+\Delta t)). \tag{4}$$

Rearranging the terms, we obtain

$$p(t+\Delta t) - p(t) = \kappa\Delta t(\gamma_h(\delta(t+\Delta t)) - p(t)), \tag{5}$$

which after dividing by Δt reduces to (2) in the limit $\Delta t \to 0$.

As an aside, we would like to make a comment on the model of partial thermalization as in Ref. [24]. The authors consider a situation in which the probability of interaction between the system and the bath is fixed. If we were to do the same, then we would have to replace $\kappa\Delta t$ by a constant, let us say λ. Then (5) would yield

$$p(t+\Delta t) - p(t) = \lambda(\gamma_h(\delta(t+\Delta t)) - p(t)), \tag{6}$$

which in the limit $\Delta t \to 0$ would simply give

$$p(t) = \gamma_h(\delta(t+\Delta t)). \tag{7}$$

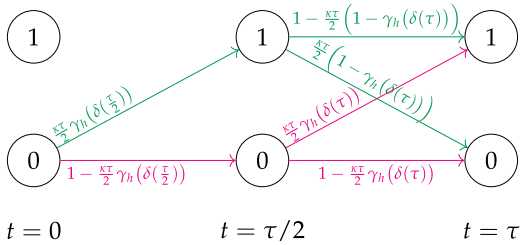
This implies that the system would be in the thermal Gibbs state at each infinitesimal step of the process. Naturally, one would obtain an isothermal reversible process with no fluctuations.

So, given that we have a general work extraction process involving partial thermalizations, let us make the following assumption in order to completely specify the model:

Assumption 1. The energy gap $\delta(t)$ is driven at a constant rate.

We are now ready to derive the results. But before we move on, let us first look at an example of a discrete version of this problem for an intuitive understanding of the underlying Markov process, which would also inform our derivations in Sec. III B.

Example 1. Let $\epsilon = \delta_{\max} - \delta_{\min}$ be the range over which we can vary δ as a function of time t, and let us choose $\delta(0) = \delta_{\max}$. Let $p(0)$ to be a constant p_0, and let the total time of the process be τ. Then, $\delta(\tau) = \delta_{\min}$ and $p(\tau)$ would be determined by Lemma 1. Now, a work extraction process involving partial thermalization corresponds to a curve on the δ-p plane. The discretization of this process is a discretization of that curve. So, let us divide the range ϵ for δ into $L = 2$ equal steps. Then, the change in δ at each step would be $\Delta\delta = -\epsilon/2$ and the extracted work during each step would be $w_{\text{ex}} = \epsilon/2$. Moreover, Assumption 1 under the above boundary conditions gives $d\delta/dt = -\epsilon/\tau$, which implies that $\Delta t = \tau/2$ for each step. Each of these discrete steps itself is composed of two steps: a level transformation and then a partial thermalization. Let us say that the system is in the ground state at time $t = 0$; see the Markov chain in Fig. 2. Clearly, since the system starts in the ground state, the work done in the first step during the level transformation denoted by $w^{t=\tau/2}$ is zero; see the first row in the second column of the table. Next, the system thermalizes with respect to the hot bath with probability $\kappa\tau/2$. The work done during this partial thermalization is dissipated as heat and thus its contribution is zero. Upon partial thermalization, we might transition to the excited state or remain in the ground state. The two possible paths are shown in the Markov chain in Fig. 2. If we transition to the excited state, then the work done during the level transformation in the second step denoted by $w^{t=\tau}$ would be $\epsilon/2$; see the second row in the fourth column. In the end, partial thermalization in the second step would again lead to two different paths with zero work contributions. A complete distribution can be obtained by going through all such paths, which are listed in the table in Fig. 2.



state at $t=0$	$w^{t=\tau/2}$	state at $t=\tau/2$	$w^{t=\tau}$	w_{ex}	$\Pr[W_{ex}=w_{ex}]$
0	0	0	0	0	$(1-p_0)\left(1-\frac{\kappa\tau}{2}\gamma_h(\delta(\frac{\tau}{2}))\right)$
0	0	1	$\epsilon/2$	$\epsilon/2$	$(1-p_0)\frac{\kappa\tau}{2}\gamma_h(\delta(\frac{\tau}{2}))$
1	$\epsilon/2$	0	0	$\epsilon/2$	$p_0\frac{\kappa\tau}{2}\left(1-\gamma_h(\delta(\frac{\tau}{2}))\right)$
1	$\epsilon/2$	1	$\epsilon/2$	ϵ	$p_0\left(1-\frac{\kappa\tau}{2}(1-\gamma_h(\delta(\frac{\tau}{2})))\right)$

FIG. 2. The Markov chain above shows two specific paths corresponding to the work extraction process given in Example 1, where the ground and excited states of the two-level system are denoted by 0 and 1, respectively. Each arrow is labeled by the corresponding transition probability. The table lists all possible paths for such a process, with each row corresponding to a specific path. The first and third columns denote the state of the system at the beginning of each step, which determines the work done during that step, namely $w^{t=\tau/2}$ and $w^{t=\tau}$ in the second and the fourth columns, respectively. $W_{\rm ex}$ is the random variable for extracted work and takes values $w_{\rm ex}$, which is the sum of work done at each step along a given path. $\Pr(W_{\rm ex}=w_{\rm ex})$ is the probability that $W_{\rm ex}$ takes the value $w_{\rm ex}$ and can be obtained using the transition probabilities for each step, as shown in Fig. 1.

III. ANALYTICAL RESULTS

In this section, we derive an expression for average work done during work extraction processes involving partial thermalizations (Sec. III A), and we prove that they are *not* fluctuation-free in general (Sec. III B).

A. Average work

Let us denote the work done during a general thermodynamic process by the random variable W. Work is done when a two-level system is in the excited state during a level transformation. Depending upon whether this transformation decreases or increases the energy gap, one obtains negative or positive values of W corresponding to a net work gain or a net work cost. We shall denote a net work gain by the random variable W, and we refer to it as just work done unless stated otherwise. Thus, the average work done during a process in which the energy gap of the system is driven from $\delta_{\max}$ to $\delta_{\min}$ as it partially thermalizes with an ambient bath for a time τ is given by

$$\mu_W(\tau) = -\int_{\delta_{\max}}^{\delta_{\min}} p(\delta)d\delta, \tag{8}$$

where $p(\delta)$ is the probability of the system to be in the excited state when the energy gap is δ. Let us first list a few ingredients that would come in handy in deriving the main result, i.e., an expression for average work, Theorem 1.

Definition 1. Given the energy gap $\delta(t)$ of a two-level system at time $t \leqslant \tau$, we define the function

$$\mathcal{G} : t \mapsto -\sum_{n=1}^{\infty} \frac{\left(-e^{-\frac{\delta(t)}{T_h}}\right)^n}{\left(\frac{n\epsilon}{\kappa\tau T_h}+1\right)}, \tag{9}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$, κ is the thermalization rate, and T_h is the temperature of the ambient bath.

The function $\mathcal{G}$ is a monotone function in t. For δ monotonically decreasing in t, $\mathcal{G}$ monotonically increases. This follows by noting that $-e^{-\delta(t)}$ is also monotonically decreasing in t. We also make use of a few standard functions in the proofs that have been redefined in Appendix B for completeness.

Lemma 2 (Time evolution of occupation probabilities under partial thermalization). Given a two-level system undergoing a work extraction process along with partial thermalizations with a bath at temperature T_h as per Assumption 1 such that its energy gap changes from $\delta_{\max}$ to $\delta_{\min}$ over a time τ, the occupation probability for the excited state at any time $0 < t < \tau$ is given by

$$p(t) = p_0 e^{-\kappa t} + \mathcal{G}(t) - e^{-\kappa t}\mathcal{G}(0), \tag{10}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$, $p_0 = p(0)$, and $\delta(t) = \delta_{\max} - \epsilon t/\tau$.

Proof. Rewriting the differential equation for a general work extraction with partial thermalizations, (2), we have

$$\frac{dp}{dt} + \kappa p(t) = \kappa\gamma_h(\delta(t)), \tag{11}$$

which can be integrated along with the initial condition $p(0) = p_0$ to obtain

$$p(t) = p_0 e^{-\kappa t} + \kappa e^{-\kappa t}\int_0^t e^{\kappa t'}\gamma_h(\delta(t'))\,dt'. \tag{12}$$

Given Assumption 1 and the boundary conditions $\delta(0) = \delta_{\max}$ and $\delta(\tau) = \delta_{\min}$, we have

$$\delta(t) = \delta_{\max} - \frac{\epsilon}{\tau}t, \tag{13}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$. Plugging $\gamma_h(\delta(t)) = \frac{1}{1+e^{\delta(t)/T_h}}$ and (13) in (12), we obtain

$$p(t) = p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \int_0^t \frac{e^{\kappa t'}}{1 + e^{\frac{(\delta_{\max} - \epsilon t'/\tau)}{T_h}}}\, dt'. \tag{14}$$

The integral above is given in terms of the hypergeometric function as in (B1). Thus,

$$\begin{aligned} p(t) &= p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \left\{ \frac{e^{(\kappa + \frac{\epsilon}{\tau T_h})t' - \frac{\delta_{\max}}{T_h}}}{\kappa + \frac{\epsilon}{\tau T_h}} \right. \\ &\quad \left. \times {}_2F_1\left(1, \frac{\kappa\tau T_h}{\epsilon} + 1, \frac{\kappa\tau T_h}{\epsilon} + 2; -e^{-\frac{(\delta_{\max} - \epsilon t'/\tau)}{T_h}}\right)\right|_0^t \Bigg\} \\ &= p_0 e^{-\kappa t} + \frac{\kappa\tau T_h}{\epsilon} \left\{ \frac{e^{-\frac{(\delta_{\max} - \epsilon t/\tau)}{T_h}}}{\frac{\kappa\tau T_h}{\epsilon} + 1} \right. \\ &\quad \times {}_2F_1\left(1, \frac{\kappa\tau T_h}{\epsilon} + 1, \frac{\kappa\tau T_h}{\epsilon} + 2; -e^{-\frac{(\delta_{\max} - \epsilon t/\tau)}{T_h}}\right) \\ &\quad - e^{-\kappa t} \frac{e^{-\frac{\delta_{\max}}{T_h}}}{\frac{\kappa\tau T_h}{\epsilon} + 1} \\ &\quad \left. \times {}_2F_1\left(1, \frac{\kappa\tau T_h}{\epsilon} + 1, \frac{\kappa\tau T_h}{\epsilon} + 2; -e^{-\frac{\delta_{\max}}{T_h}}\right)\right\}. \end{aligned} \tag{15}$$

Next, using (B2), we can write

$$\begin{aligned} &\left(\frac{az}{a+1}\right) {}_2F_1(1, 1+a, 2+a; -z) \\ &\quad = \left(\frac{az}{a+1}\right) \sum_{n=0}^{\infty} \frac{n!(1+a)_n}{(2+a)_n} \frac{(-z)^n}{n!} \\ &\quad = -\sum_{n'=1}^{\infty} \frac{(-z)^{n'}}{\left(\frac{n'}{a} + 1\right)}. \end{aligned} \tag{16}$$

Using (16) we can write (15) in terms of the function $\mathcal{G}$, Definition 1, to obtain (10).

We are now ready to derive the expression for average work.

Theorem 1 (Average work). The average work done by a two-level system during a work extraction process involving partial thermalizations with respect to a bath at temperature T_h, wherein its energy gap is driven from $\delta_{\max}$ to $\delta_{\min}$ as per Assumption 1 over a time τ, is given by

$$\begin{aligned} \mu_W(\tau) = W_{\text{iso}}^{T_h} &+ \frac{W_{\text{ad}}}{\kappa\tau}(1 - e^{-\kappa\tau}) \\ &- \frac{\epsilon}{\kappa\tau}\{\mathcal{G}(\tau) - e^{-\kappa\tau}\mathcal{G}(0)\}, \end{aligned} \tag{17}$$

where $W_{\text{iso}}^{T_h}$ is the work done during the corresponding isothermal process, i.e., $W_{\text{iso}}^{T_h} = T_h \ln\left(Z(\delta_{\min})/Z(\delta_{\max})\right)$, with Z being the partition function $Z : \delta \mapsto 1 + e^{-\delta/T_h}$, W_{ad} is the work done during the corresponding adiabatic process, i.e., $W_{\text{ad}} = \epsilon p_0$, where $p_0 = p(0)$, and $\epsilon = \delta_{\max} - \delta_{\min}$.

Proof. We start by noting that

$$\frac{dp}{d\delta} = \frac{dp}{dt}\frac{dt}{d\delta} = -\frac{\kappa\tau}{\epsilon}(\gamma_h(\delta) - p), \tag{18}$$

where the last line follows from (2) and (13) and suppressing the dependence on t. Integrating (18) with respect to δ from $\delta_{\max}$ to $\delta_{\min}$, we have

$$\int_{\delta_{\max}}^{\delta_{\min}} p\, d\delta = \int_{\delta_{\max}}^{\delta_{\min}} \gamma_h(\delta) d\delta + \frac{\epsilon}{\kappa\tau} \int_{\delta_{\max}}^{\delta_{\min}} \frac{dp}{d\delta} d\delta. \tag{19}$$

Then, plugging (19) in (8) implies

$$\mu_W(\tau) = -\int_{\delta_{\max}}^{\delta_{\min}} \gamma_h(\delta) d\delta - \frac{\epsilon}{\kappa\tau} \int_{\delta_{\max}}^{\delta_{\min}} \frac{dp}{d\delta} d\delta. \tag{20}$$

Substituting the expression for $\gamma_h(\delta)$ and evaluating the integral gives us the first term of (20) as

$$\int_{\delta_{\max}}^{\delta_{\min}} \gamma_h(\delta) d\delta = -T_h \ln \frac{Z(\delta_{\min})}{Z(\delta_{\max})}, \tag{21}$$

where Z is the partition function. The expression above is simply the negative of the work done during the corresponding isothermal reversible process,

$$W_{\text{iso}}^{T_h} = T_h \ln \frac{Z(\delta_{\min})}{Z(\delta_{\max})}. \tag{22}$$

Next, we evaluate the integral in the second term in (20) using Lemma 2 together with the boundary conditions $p(\delta_{\max}) = p_0$ and $p(\delta_{\min}) = p(\tau)$. Thus, we have

$$\begin{aligned} \int_{\delta_{\max}}^{\delta_{\min}} \frac{dp}{d\delta}\, d\delta &= p(\delta_{\min}) - p(\delta_{\max}) \\ &= p_0(e^{-\kappa\tau} - 1) + \mathcal{G}(\tau) - e^{-\kappa t}\mathcal{G}(0). \end{aligned} \tag{23}$$

Now, if one changes the energy gap from $\delta_{\max}$ to $\delta_{\min}$ adiabatically, the distribution of work is simply a two-point distribution, where $W = 0$ occurs with probability $1 - p_0$, and $W = \epsilon$ occurs with probability p_0. Thus, the average work done would be

$$W_{\text{ad}} = \epsilon p_0. \tag{24}$$

Plugging (21) and (23) in (20) together with (22) and (24) gives us the following result.

Corollary 1. The expression for average work in Theorem 1 reduces to the adiabatic case in the limit $\tau \to 0$, i.e.,

$$\lim_{\tau\to 0} \mu_W(\tau) = W_{\text{ad}}, \tag{25}$$

and the isothermal case in the limit $\tau \to \infty$,

$$\lim_{\tau\to\infty} \mu_W(\tau) = W_{\text{iso}}^{T_h}. \tag{26}$$

Proof. Let us first derive the adiabatic limit, $\tau \to 0$:

$$\begin{aligned} \lim_{\tau\to 0} \mu_W(\tau) = W_{\text{iso}}^{T_h} + \lim_{\tau\to 0} \left\{ \frac{W_{\text{ad}}}{\kappa\tau}(1 - e^{-\kappa\tau}) \right. \\ \left. + \frac{\epsilon}{\kappa\tau}(\mathcal{G}(\tau) - e^{-\kappa\tau}\mathcal{G}(0)) \right\}. \end{aligned} \tag{27}$$

Let us first look at the second term in the limit

$$\lim_{\tau\to 0}\frac{1}{\tau}(1-e^{-\kappa\tau}) = \lim_{\tau\to 0}\frac{1}{\tau}\left(1-\left(1-\kappa\tau+\frac{\kappa^2\tau^2}{2}-\cdots\right)\right)$$
$$= \lim_{\tau\to 0}\left(\kappa-\frac{\kappa^2\tau}{2}+\cdots\right)=\kappa. \tag{28}$$

So, we have

$$\lim_{\tau\to 0}\mu_W(\tau) = W_{\text{iso}}^{T_h}+W_{\text{ad}}+\lim_{\tau\to 0}\frac{\epsilon}{\kappa\tau}\{\mathcal{G}(\tau)-e^{-\kappa\tau}\mathcal{G}(0)\}$$
$$= W_{\text{iso}}^{T_h}+W_{\text{ad}}+T_h\Big\{-e^{-\frac{\delta_{\min}}{T_h}}\,\Phi_L\Big(-e^{-\frac{\delta_{\min}}{T_h}},1,1\Big)$$
$$+e^{-\frac{\delta_{\max}}{T_h}}\,\Phi_L\Big(-e^{-\frac{\delta_{\max}}{T_h}},1,1\Big)\Big\}, \tag{29}$$

where we have used Definition B.2 in the second step. Since $z\Phi_L(z,1,1) = -\ln(1-z)$, we have

$$\lim_{\tau\to 0}\mu_W(\tau) = W_{\text{iso}}^{T_h}+W_{\text{ad}}+T_h\Big\{\ln\Big(1+e^{-\frac{\delta_{\min}}{T_h}}\Big)$$
$$-\ln\Big(1+e^{-\frac{\delta_{\max}}{T_h}}\Big)\Big\}, \tag{30}$$

where the first term cancels the third term due to (21), and thus we obtain (25). The isothermal limit, $\tau\to\infty$, can be similarly obtained since

$$\lim_{\tau\to\infty}\mu_W(\tau) = W_{\text{iso}}^{T_h}-\lim_{\tau\to\infty}\left\{-\frac{W_{\text{ad}}}{\kappa\tau}(1-e^{-\kappa\tau})\right.$$
$$\left.+\frac{\epsilon}{\kappa\tau}(\mathcal{G}(\tau)-e^{-\kappa\tau}\mathcal{G}(0))\right\}, \tag{31}$$

and it is clear that the second term in the equation above would vanish in the limit $\tau\to\infty$. Furthermore, using Definition 1, we find that the third term would also vanish in the limit, and so we recover (26).

B. Lower bound on variance

We will now establish, by means of the following theorem, that fluctuations in work during processes involving partial thermalizations are nonzero, independent of Assumption 1.

Theorem 2 (Fluctuations in work). Consider a two-level system undergoing a work extraction process where the energy gap is driven from $\delta_{\max}$ to $\delta_{\min}$ in L discrete steps along with partial thermalizations over a finite time τ. Then, the following are true in general for the random variable W_L denoting the total work done during such a process:

$$\lim_{L\to\infty}\Pr(W_L=0) = (1-p_0)e^{-\kappa\int_0^\tau dt\,\gamma_h(\delta(t))} \tag{32}$$

and

$$\lim_{L\to\infty}\Pr(W_L=\epsilon) = p_0 e^{-\kappa\int_0^\tau dt[1-\gamma_h(\delta(t))]}, \tag{33}$$

where $\epsilon=\delta_{\max}-\delta_{\min}$, $L\to\infty$ is the continuous time limit, and p_0 is the initial excited-state probability of the two-level system.

Proof. From Fig. 2, it is easy to see that the following expression holds for a discrete partial thermalization process composed of L steps such that each step takes time Δt:

$$\Pr(W_L=0) = (1-p_0)\prod_{l=1}^{L-1}(1-\kappa\Delta t\,\gamma_h(\delta(l\Delta t))). \tag{34}$$

Taking log on both sides of the above equation, we have

$$\ln(\Pr(W_L=0)) = \ln(1-p_0)$$
$$+\sum_{l=1}^{L-1}\ln(1-\kappa\Delta t\,\gamma_h(\delta(l\Delta t)))$$
$$\overset{\Delta t\ll 1}{\simeq}\ln(1-p_0)$$
$$-\kappa\sum_{l=1}^{L-1}\Delta t\,\gamma_h(\delta(l\Delta t)). \tag{35}$$

Taking the limit $\Delta t\to 0$ ($L\to\infty$) and observing that the second term above would thus be a Riemann sum, we obtain (32) by exponentiating the resulting expression (and noting that limit commutes with continuous functions). Similarly, the last row in Fig. 2 implies that

$$\Pr(W_L=\epsilon) = p_0\prod_{l=1}^{L-1}(1-\kappa\Delta t[1-\gamma_h(\delta(l\Delta t))]). \tag{36}$$

Again, taking log on both sides, we have

$$\ln(\Pr(W_L=\epsilon))$$
$$=\ln p_0+\sum_{l=1}^{L-1}\ln[1-\kappa\Delta t(1-\gamma_h(\delta(l\Delta t)))]$$
$$\overset{\Delta t\ll 1}{\simeq}\ln p_0-\kappa\sum_{l=1}^{L-1}\Delta t(1-\gamma_h(\delta(l\Delta t))). \tag{37}$$

Again, taking the limit $\Delta t\to 0$ ($L\to\infty$) results in an expression that gives (33) upon exponentiation.

This result analytically establishes that the distribution of work is typically broad, as was also found numerically in Ref. [23]. While the theorem above holds in general, a lower bound on the variance of work done by systems driven linearly in time (Assumption 1) can be obtained as a corollary to it.

Corollary 2 (Lower bound on variance of work). For a finite-time process as per Assumption 1 along with partial thermalizations, the variance of work is bounded from below as

$$\sigma_W^2(\tau)\geqslant(1-p_0)\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}\mu_W^2(\tau)$$
$$+p_0\,e^{-\kappa\tau}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{\frac{\kappa\tau T_h}{\epsilon}}(\epsilon+\mu_W(\tau))^2, \tag{38}$$

where Z is the partition function $Z:\delta\mapsto 1+e^{-\delta/T_h}$, and $\mu_W(\tau)$ is the average work output of the process as given by Theorem 1. Moreover, the lower bound is saturated in the adiabatic limit,

$$\lim_{\tau\to 0}\sigma_W^2(\tau) = p_0(1-p_0)\epsilon^2, \tag{39}$$

as well as in the isothermal limit,

$$\lim_{\tau\to\infty}\sigma_W^2(\tau)=0. \tag{40}$$

Proof. We will first derive expressions for the probabilities of work values $W=0$ and $W=\epsilon$ when undergoing a finite-time process per Assumption 1 along with partial thermalizations using Theorem 2. Using the expression for $\delta(t)$ as given by (13), we change the variable of integration to δ in (32) and obtain the following after taking log on both sides:

$$\lim_{L\to\infty}\ln(\Pr(W_L=0)) = \ln(1-p_0)+\frac{\kappa\tau}{\epsilon}\int_{\delta_{\max}}^{\delta_{\min}}\frac{d\delta}{1+e^{\delta/T_h}}. \tag{41}$$

Evaluating the integral and exponentiating the above, we have

$$\lim_{L\to\infty}\Pr(W_L=0)=(1-p_0)\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}, \tag{42}$$

where Z is the partition function. Similarly, (33) gives

$$\lim_{L\to\infty}\ln(\Pr(W_L=\epsilon)) = \ln p_0+\frac{\kappa\tau}{\epsilon}\int_{\delta_{\max}}^{\delta_{\min}}\frac{d\delta}{1+e^{-\delta/T_h}}. \tag{43}$$

Again, evaluating the integral and exponentiating the above, we obtain

$$\lim_{L\to\infty}\Pr(W_L=\epsilon)=p_0\,e^{-\kappa\tau}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{\frac{\kappa\tau T_h}{\epsilon}}. \tag{44}$$

Now that we have the expressions for $\Pr(W_L=0)$ and $\Pr(W_L=\epsilon)$, it is straightforward to obtain a lower bound for the variance of work as the sum of these two contributions. Thus,

$$\sigma_{W_L}^2(\tau)\geqslant\Pr(W_L=0)(\mu_{W_L}(\tau))^2+\Pr(W_L=\epsilon)(\epsilon-\mu_{W_L}(\tau))^2. \tag{45}$$

Taking the limit $L\to\infty$ and assuming that W_L converges in probability to the random variable W for the continuous process, we have

$$\sigma_W^2(\tau)\geqslant\lim_{L\to\infty}\{\Pr(W_L=0)(\mu_W(\tau))^2+\Pr(W_L=\epsilon)(\epsilon-\mu_W(\tau))^2\}. \tag{46}$$

Plugging (42) and (44) in the equation above gives (38). Let us now look at the lower bound in the following two limiting cases.

(i) Adiabatic limit, $\tau\to 0$:

$$\begin{aligned}\lim_{\tau\to0}&\left\{(1-p_0)\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}\mu_W^2(\tau)\right.\\&\left.+p_0\,e^{-\kappa\tau}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{\frac{\kappa\tau T_h}{\epsilon}}(\epsilon-\mu_W(\tau))^2\right\}\\&=\lim_{\tau\to0}\left\{(1-p_0)\mu_W^2(\tau)+p_0(\epsilon-\mu_W(\tau))^2\right\}\\&=p_0(1-p_0)\epsilon^2,\end{aligned} \tag{47}$$

where the last line follows from (25). Recall that the average work done when changing the energy gap from $\delta_{\max}$ to $\delta_{\min}$ adiabatically is given by (24). Moreover, the variance of work for an adiabatic process can be obtained by noting that the distribution of $W_{\text{ad}}\in\{0,\epsilon\}$ is simply $\{1-p_0,p_0\}$, i.e.,

$$\begin{aligned}\sigma_W^2(\tau=0)&=p_0(\epsilon-W_{\text{ad}})^2+(1-p_0)W_{\text{ad}}^2\\&=p_0(1-p_0)\epsilon^2.\end{aligned} \tag{48}$$

Therefore, (47) and (48) together imply that the lower bound is saturated in said limit.

(ii) Isothermal limit, $\tau\to\infty$:

$$\begin{aligned}\lim_{\tau\to\infty}&\left\{(1-p_0)\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}\mu_W^2(\tau)\right.\\&\left.+p_0\,e^{-\kappa\tau}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{\frac{\kappa\tau T_h}{\epsilon}}(\epsilon-\mu_W(\tau))^2\right\}.\end{aligned} \tag{49}$$

Now, let us look at the relevant part in the first term of (49). Plugging in the definition for the partition function Z, we have

$$\lim_{\tau\to\infty}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}=\lim_{\tau\to\infty}\left(\frac{1+e^{-\delta_{\min}/T_h}}{1+e^{-\delta_{\max}/T_h}}\right)^{-\frac{\kappa\tau T_h}{\epsilon}}=0 \tag{50}$$

as $1+e^{-\delta_{\min}/T_h}>1+e^{-\delta_{\max}/T_h}$. Similarly, we look at the relevant part of the second term in (49) to obtain

$$\begin{aligned}\lim_{\tau\to\infty}&e^{-\kappa\tau}\left(\frac{Z(\delta_{\min})}{Z(\delta_{\max})}\right)^{\frac{\kappa\tau T_h}{\epsilon}}\\&=\lim_{\tau\to\infty}\left[e^{-\epsilon/T_h}\left(\frac{1+e^{-\delta_{\min}/T_h}}{1+e^{-\delta_{\max}/T_h}}\right)\right]^{\frac{\kappa\tau T_h}{\epsilon}}\\&=\lim_{\tau\to\infty}\left(\frac{1+e^{\delta_{\min}/T_h}}{1+e^{\delta_{\max}/T_h}}\right)^{\frac{\kappa\tau T_h}{\epsilon}}\\&=0,\end{aligned} \tag{51}$$

where we have used the fact that $\epsilon=\delta_{\max}-\delta_{\min}$ along with $1+e^{\delta_{\min}/T_h}<1+e^{\delta_{\max}/T_h}$. Thus, we obtain

$$\lim_{\tau\to\infty}\sigma_W^2(\tau)\geqslant 0. \tag{52}$$

Moreover, from Ref. [11] we know that isothermal work extraction is fluctuation-free, i.e.,

$$\sigma_W^2(\tau=\infty)=0. \tag{53}$$

Again, (52) and (53) together imply that the lower bound is saturated in this limit.

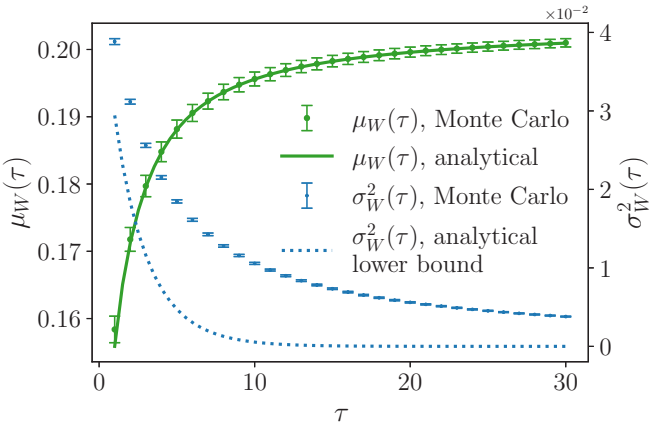


FIG. 3. On the x-axis we have the total time of the work extraction process, τ. The solid green (gray) curve interpolates between the adiabatic $W_{\text{ad}} = 0.134$ and the isothermal $W_{\text{iso}}^{T_h} = 0.204$ limits. The dashed blue (black) curve also interpolates between the adiabatic $\sigma_W^2(\tau = 0) = 0.049$ and the isothermal $\sigma_W^2(\tau = \infty) = 0$ limits. The Monte Carlo simulations were done with $L = 1000$ steps, where L is the discretization (see Example 1) and for integer values of $\tau \in [1, 30]$. The parameter values used are $\delta_{\max} = 1$, $\delta_{\min} = 0.5$, $T_h = 2$, $p_0 = \frac{1}{1+e}$, and $\kappa = 1$.

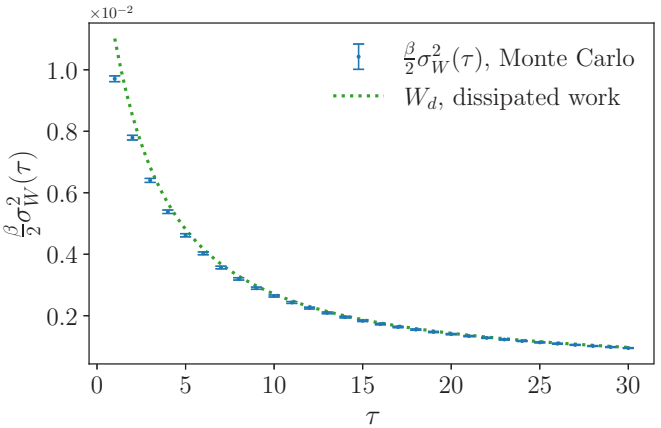


FIG. 4. Fluctuation-dissipation relation for finite-time processes. On the x-axis we have the total time of the work extraction process, τ. W_d is the dissipated work. The Monte Carlo simulations were done for $L = 1000$ steps, where L is the discretization (see Example 1) and for integer values of $\tau \in [1, 30]$. The parameter values used are $\delta_{\max} = 1$, $\delta_{\min} = 0.5$, $T_h = 2$, $p_0 = \frac{1}{1+e^{1/2}}$, and $\kappa = 1$.

IV. NUMERICAL RESULTS

In this section, we present the results of the Monte Carlo simulation for the Markov process, Fig. 1, to obtain estimates of the variance as a function of the time period of the process. Furthermore, for a two-level system that is initially in equilibrium with the bath, we find that the variance can be estimated using Jarzynski's fluctuation-dissipation relation.

A. Monte Carlo for variance of work

To compare the gap between the analytical lower bound obtained in Corollary 2 with the actual variance, we perform Monte Carlo simulations since an analytical derivation seems to be intractable due to the time-dependent nature of the Markov process, Fig. 1. The Monte Carlo basically simulates a discrete version of the Markov process under Assumption 1; see Example 1. We plot the results of the same in Fig. 3. As a test of credibility, we find that the error bars on our numerically obtained values of average work successfully envelop the analytical form as a function of τ (Theorem 1). The error bars were obtained using 10^4 independent runs. The independent runs were parallelized using GNU parallel [26].

B. Fluctuation-dissipation relation

A fluctuation-dissipation relation governing an irreversible thermodynamic process is a statement about the relation between the dissipated work (on average) when a system is driven away from equilibrium and the corresponding fluctuations of work during such a process. Jarzynski's [3] much touted result gave such a relation in the weak system-bath interaction limit. Basically, once the system is in equilibrium with the ambient bath, it is disconnected from the bath and then the work extraction process is performed, which essentially amounts to changing the value of some relevant parameter (that governs the Hamiltonian) over a finite amount of time. When the time over which the process is carried out—the switching time—is large enough, it renders the distribution of work Gaussian, and the fluctuation-dissipation relation follows. Denoting the random variable for the work done during such an irreversible process by W and its mean and variance by μ_W and σ_W^2, respectively, the dissipated work is $W_{\text{diss}} = \mu_W - \Delta F$, the difference between the average work done during the process, μ_W, and the average work done during the corresponding reversible process, i.e., the free-energy difference, ΔF. The fluctuation-dissipation relation can then be expressed as

$$W_{\text{diss}} = \frac{\beta}{2}\sigma_W^2, \tag{54}$$

where $\beta = 1/k_B T_h$, with T_h being the temperature of the ambient bath. This relation has been generalized [27,28] to the case in which the system continues to be in contact with the bath during the work extraction process. Using Theorem 1 with $p_0 = 1/(1 + e^{\delta_{\max}/T_h})$, we plot the dissipated work, $\mu_W(\tau) - \Delta F$, and the estimate of the variance from the Monte Carlo simulation as a function of the total time period of the process τ in Fig. 4. We observe that the dissipated work provides an upper bound for the variance of work in general. This bound is saturated in the limit of large τ, in agreement with the aforementioned result of Refs. [27,28].

V. APPLICATION TO FINITE-TIME HEAT ENGINES

Finite-time heat engines are characterized by their nonzero power output in contrast to the ideal Carnot engine. In this section, we discuss finite-time heat engines operating in cycles that are composed of work extraction processes involving partial thermalizations and instantaneous adiabatic energy-level transformations. First, we review the Carnot engine for a classical two-level system in Sec. V A, and then we study one such engine that incorporates work extraction processes mediated by partial thermalizations replacing the ideal isothermal

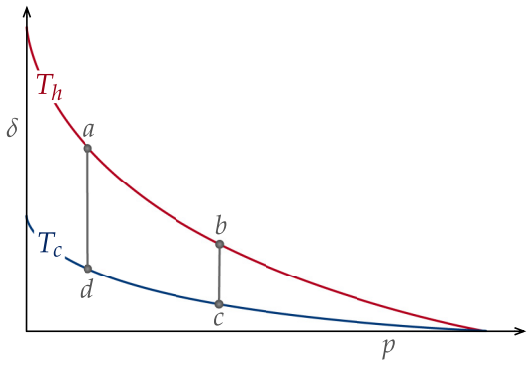


FIG. 5. Carnot cycle for a two-level system with energy gap δ and excited-state occupation probability p.

processes of the Carnot cycle in Sec. V B. We then optimize the power output of such cycles for fixed time periods over different sets of parameters and constraints in Sec. V B 1 and V B 2. Finally, we compare the two in Sec. V C.

A. Carnot engine: Review

Let us assume that we have access to a hot bath at temperature T_h, a cold bath at temperature T_c, and a two-level system whose energy gap δ can be varied over a fixed range between $\delta_{\min}$ and $\delta_{\max}$. And, let the occupation probability for the excited state be denoted by p. As done earlier, let us set the ground-state energy of the system to be zero. We use the formalism of Ref. [29], where a Carnot engine was studied in the quantum context, but it also applies to our case. Thus, a Carnot cycle is composed of four stages that can be defined using points a, b, c, d on the p-δ plot for a two-level system, Fig. 5. First, we have the following:

(i) $a \mapsto b$, an isothermal expansion: at point a, the system is in a Gibbs-thermal state at temperature T_h with an energy gap δ_a. The occupation probability for the excited state is $p_a = \frac{1}{1+e^{\delta_a/T_h}}$. During an isothermal expansion in a two-level system, the energy levels must change such that they are scaled by the same factor $k_1 < 1$; see Appendix A for proof. The state of the system at point b is a Gibbs state at temperature T_h with an energy gap $\delta_b = k_1\delta_a$. As has been shown in Ref. [11], the work done during such a reversible isothermal process is essentially *deterministic*, and it is given by

$$W_{ab} = T_h \ln \frac{Z(\delta_b)}{Z(\delta_a)}, \tag{55}$$

where Z is the partition function.

(ii) Then, $b \mapsto c$, an adiabatic process: during an adiabatic process, the energy levels of the system change without any accompanying change in occupation probabilities. In particular, at this stage the energy levels are changed by a factor such that the system is in the Gibbs state with respect to the cold bath at temperature T_c, implying

$$\frac{\delta_b}{T_h} = \frac{\delta_c}{T_c}. \tag{56}$$

Thus, the energy gap of the system at point c is $\delta_c = T_h/T_c\ k_1\delta_a$. The work done in this process, W_{bc}, is a *random variable* as it depends on the state of the system at point b [30]. The average value of the work done during this process is

$$\overline{W}_{bc} = \frac{1}{1+e^{\delta_c/T_c}}(\delta_b - \delta_c). \tag{57}$$

(iii) Next, the compression stage with $c \mapsto d$, an isothermal compression: again, during this process the energy levels are scaled by a factor $k_2 > 1$. So, the system is still in a Gibbs-thermal state with respect to the cold bath at temperature T_c at point d but with an energy gap $\delta_d = T_h/T_c\ k_1k_2\delta_a$. The work cost of this process is deterministic and is given by

$$W_{cd} = -T_c \ln \frac{Z(\delta_d)}{Z(\delta_c)}. \tag{58}$$

(iv) Finally, we have $d \mapsto a$, an adiabatic process where the energy gap is changed such that we go back to the starting point a with energy gap δ_a and $p_d = p_a$. Therefore,

$$\frac{\delta_d}{T_c} = \frac{\delta_a}{T_h}. \tag{59}$$

But, $\delta_d = T_h/T_c\ k_1k_2\delta_a$. This implies that the constant k_2 is not independent but must satisfy the relation $k_2 = \frac{1}{k_1}$. The average work cost of this process is

$$\overline{W}_{da} = \frac{1}{1+e^{\delta_a/T_h}}(\delta_a - \delta_d). \tag{60}$$

The total work done during the Carnot cycle, denoted by the random variable W_C, is just the sum of work done at each stage, and it is given by

$$W_C = W_{ab} + W_{bc} - W_{cd} - W_{da}. \tag{61}$$

The distribution of work and expected efficiency of the Carnot engine can then be obtained as stated in the following lemma, whose proof can be found in Appendix C:

Lemma 3. The total work done during a microscopic implementation of the Carnot cycle is a random variable W_C distributed according to a four-point distribution listed in the table below.

w_C	$\Pr(W_C = w_C)$
$(T_h - T_c)\ln Z(\delta_b)/Z(\delta_a)+0$	$(1-p_a)(1-p_b)$
$(T_h - T_c)\ln Z(\delta_b)/Z(\delta_a) - (\delta_a - \delta_d)$	$(1-p_b)p_a$
$(T_h - T_c)\ln Z(\delta_b)/Z(\delta_a) + \delta_b - \delta_c$	$(1-p_a)p_b$
$(T_h - T_c)\ln Z(\delta_b)/Z(\delta_a) + \delta_b - \delta_c - \delta_a + \delta_d$	p_bp_a

The expected efficiency of the Carnot cycle is

$$\eta_C^{\text{avg}} = \left(1 - \frac{T_c}{T_h}\right). \tag{62}$$

Now, for the given pair of temperatures T_c and T_h, the Carnot efficiency is the maximum attainable efficiency. It is independent of the points a, b, c, and d on the p-δ plot, Fig. 5, that define a work extraction cycle for the engine connecting the two isotherms. However, there is another quantity that becomes relevant under the constraint of being able to vary the energy gap δ only between $\delta_{\min}$ and $\delta_{\max}$, the average work

output. In fact, the cycle that maximizes the average work output is the Carnot cycle that encloses the largest area on the p-δ plot—it maximizes both efficiency and average work. We state this intuition in the lemma below, deferring a formal proof to Appendix D for completeness.

Lemma 4 (Optimal Carnot cycle for average work). Given a Carnot engine formed by a classical two-level system operating between a hot bath at temperature T_h and a cold bath at temperature T_c such that the energy gap of the system δ can only be varied over a fixed range between $\delta_{\min}$ and $\delta_{\max}$, the cycle (defined by the points a, b, c, and d on the p-δ plot) that maximizes the average work output of the Carnot engine is the one for which $\delta_a = \delta_{\max}$ and $\delta_c = \delta_{\min}$.

The power output of such a cycle is zero due to the isothermal processes that require infinitely long equilibration times. But, finite-time work extraction cycles have nonzero power output, and for such cycles one is generally interested in the efficiency at maximum power [31]. We analyze such engines in the next section.

B. Finite-time heat engines

For constant time periods, maximizing power amounts to maximizing the average work output. We define a modification of the Carnot cycle that incorporates the finite-time element—replacing isothermal processes in a Carnot cycle by work extraction processes with partial thermalizations. So, a finite-time cycle denoted by $a \mapsto b \mapsto c \mapsto d \mapsto a$ on the p-δ plot constitutes a sequence of four processes. First we have the following:

(i) $a \mapsto b$, work extraction with partial thermalizations with respect to the hot bath. The coordinates of point a on the p-δ plot are $(\delta_a,\ p_a)$. The system is driven under Assumption 1 by an amount $\delta_a - \delta_{b1}$ for a time τ_1. The occupation probability for the excited state $p_b(\tau_1)$ can then be obtained using Lemma 2. Furthermore, the average work done during this process would be given by Theorem 1.

(ii) Then, $b \mapsto c$, an adiabatic process. The energy gap is changed from δ_b to δ_c keeping the occupation probabilities fixed, i.e., $p_c = p_b(\tau_1)$. The average work done during this process would be

$$\overline{W}_{bc} = p_b(\tau_1)(\delta_c - \delta_b). \tag{63}$$

(iii) Next, we have $c \mapsto d$, work extraction with partial thermalizations with respect to the cold bath. Starting from the point c with coordinates $(\delta_c,\ p_b(\tau_1))$, the system is again driven under Assumption 1 for a time τ_2 such that the energy gap increases from δ_c to δ_d. To ensure that we complete the cycle and reach point a in the end, δ_d must be such that

$$p_d(\tau_2) = p_a. \tag{64}$$

An expression for $p_{d_1}(\tau_2)$ and the average work cost of this process can be derived along the lines of Lemma 2 and Theorem 1, as done in Appendix E.

(iv) Finally, we close the loop with $d \mapsto a$ adiabatically. Having reached δ_d in accordance with (64), we complete the cycle by changing the energy gap keeping the occupation probabilities fixed. The average work cost of this process is simply

$$\overline{W}_{da} = p_a(\delta_a - \delta_d). \tag{65}$$

The time period of the cycle as described above would thus be $\mathcal{T} = \tau_1 + \tau_2$. Since we are interested in the efficiency at maximum power, we want to maximize the average work output of a finite-time cycle with a fixed time period $\mathcal{T} = \tau_1 + \tau_2$, which would simply be the sum of the average work done at each of the four steps described above. The parameters characterizing a finite-time cycle as described above are given by the set $\{\delta_a,\ p_a,\ \delta_b,\ \delta_c,\ \tau_1\}$. As $\mathcal{T} = \tau_1 + \tau_2$, only one of them can be chosen freely—let it be τ_1. The fact that for every value of τ_2 one has to solve (64) for δ_d leaves no room for analytical analysis. We perform numerical optimizations instead, setting the thermalization rates for both the processes $a \mapsto b$ and $c \mapsto d$ to be unity without loss of generality. The numerical optimizations were performed on MATHEMATICA [32] using the Nelder-Mead method [33]. First, we perform optimizations for the special case in which one can recover the Carnot cycle, Lemma 4, in the limit of large $\mathcal{T}$.

1. Optimal finite-time cycles limiting to the Carnot cycle

To recover the Carnot cycle in the limit of a large time period of a finite-time cycle, we need to fix the values of the parameters accordingly. For the first process to approach the hot isotherm, it is clear that δ_a and δ_b should be the same as in the case of the optimal Carnot cycle, Lemma 4. However, δ_c must be chosen to lie on the cold isotherm, i.e., it should satisfy the relation

$$p_b(\tau_1) = \frac{1}{1 + e^{\delta_c/T_c}}, \tag{66}$$

since only then would the third leg, i.e., $c \mapsto d$, approach the cold isotherm in the limit of large $\mathcal{T}$. This implies that we are left with only one free parameter, namely τ_1. Thus, maximizing the average work output for different values of $\mathcal{T}$ results in different optimal cycles, which we plot on the left in Fig. 6. We also plot the cumulative distribution for the different optimal cycles along with that of the Carnot cycle to study the fluctuations as we approach equilibrium in Fig. 7 (left). Note that the Carnot cycle has a four-point work distribution; see Lemma 3. The distributions for finite-time cycles are obtained by performing Monte Carlo simulations. We find that even though the average work cycles start approaching the Carnot cycle quickly, the cumulative distribution still remains smooth until we go to very large values of $\mathcal{T}$.

2. General optimal finite-time cycles

Previously we were interested in the special case that gave the Carnot cycle in the limit of large time periods. However, for the most general problem, where one has access to a hot bath at temperatures T_h and a cold one at temperature T_c, and the energy gap can only be driven between $\delta_{\max}$ and $\delta_{\min}$, one should optimize all the parameters in the set $\{\delta_a,\ p_a,\ \delta_b,\ \delta_c,\ \tau_1\}$. Here, we find that the optimal cycle in the limit of a large time period approaches a different cycle, one where the two isotherms are connected by two purely thermal processes. So, $d \mapsto a$ and $b \mapsto c$ would be thermalizations connecting the two isotherms at $d = a = \delta_{\max}$ and $\delta_b = \delta_c = \delta_{\min}$, respectively, the limiting cycle as shown in Fig. 6 on the right. This can be understood intuitively since we want to maximize work *output*—the processes in which we have to

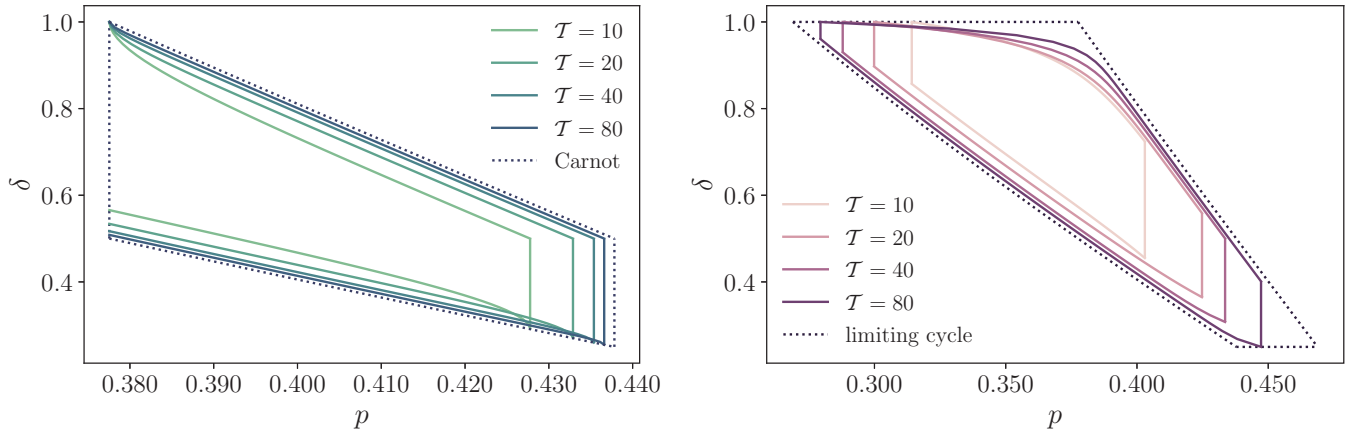


FIG. 6. The optimal finite-time cycles as obtained in Sec. V B. On the x-axis we have occupation probability for the excited state p. On the y-axis we have the energy gap δ. We use parameters $\delta_{\max} = 1$, $\delta_{\min} = 0.25$, $T_h = 2$, and $T_c = 1$. On the left we have optimal cycles as obtained in Sec. V B 1 with $\delta_a = \delta_{\max}$ and $\delta_b = 2\delta_{\min}$. On the right we have optimal cycles from Sec. V B 2.

perform work are not favorable. As the work output of an adiabatic process is less than that of the corresponding isothermal process (and vice versa for the work input), the adiabatic legs are completely lost and get replaced by isothermal extensions. Even though this cycle is not very relevant from the point of view of power maximization, as for large time periods power is no longer a meaningful metric, it is worth noting the curious form of the cycle in contrast to the corresponding maximum efficiency cycle—the Carnot cycle. We plot the optimal cycles for different values of time periods $\mathcal{T}$ in Fig. 6 (right) along with the cumulative distributions in Fig. 7 (right).

C. Comparing finite-time optimal cycles

First, we compare the two scenarios discussed above in terms of their cumulative distributions, and we find that the general optimal cycles have a better quality of work—fewer fluctuations. For example, in Fig. 8 we plot the distributions for $\mathcal{T} = 10$, and we observe that the cumulative distribution for the solution of the general optimum problem crosses the one obtained in Sec. V B 1 around $w = 0$ and lies below it for almost all negative values of w. This means that the probability with which one has to input work in the former case is always less than the latter. Intuitively, there is no real reason to constrain the parameter values as we did in Sec. V B 1 other than the imposed restriction of recovering the Carnot cycle in the limit of large $\mathcal{T}$. This limit is not particularly interesting from the point of view of maximizing power as it vanishes in said limit. However, such a comparison is at the level of fluctuations only. Next, we compare P^*, the maximum power itself as a function of $\mathcal{T}$ for the two cases in Fig. 9, and we find that the general optimal power is higher than the corresponding power from optimal cycles that approach the Carnot cycle in the limit of large time periods. This is what one would expect anyway as the latter is a restricted version of the general optimization problem, Sec. V B 2.

Figures 8 and 9 together imply that the general optimal cycles are better as far as power output and fluctuations are concerned. Finally, we compare the optimal efficiencies η^* for the two scenarios as a function of $\mathcal{T}$ in Fig. 10, and we find that the optimal cycles that approach the Carnot cycle in the limit of large time period $\mathcal{T}$ have much higher efficiencies

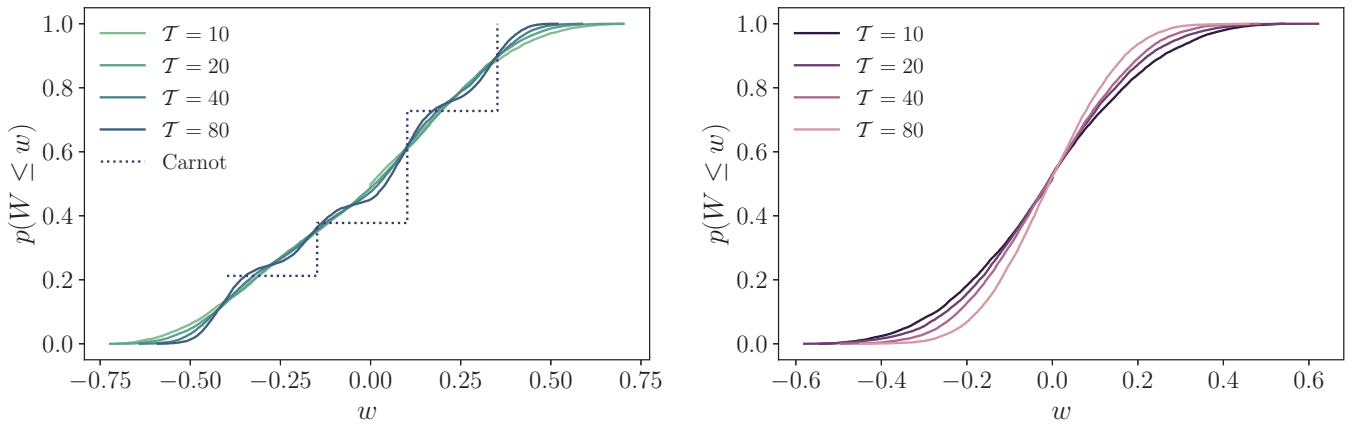


FIG. 7. The cumulative distribution function for the random variable W, the work extracted during different optimal cycles (different values of $\mathcal{T}$) as obtained in Sec. V B. On the x-axis we have the possible work values. The Monte Carlo simulations were performed for 10^4 samples for each of the optimum cycles. On the left is the distribution for optimal cycles as obtained in Sec. V B 1, where $\delta_a = \delta_{\max}$ and $\delta_b = 2\delta_{\min}$. On the right is the distribution for optimal cycles from Sec. V B 2.

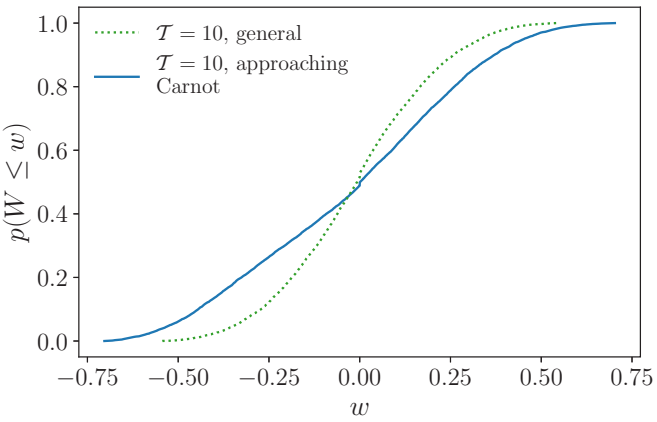


FIG. 8. Comparing cumulative distribution of work for optimal cycles obtained in Sec. V B 1 and Sec. V B 2. On the x-axis we have the possible work values. Negative values of w imply a net work input.

compared to the optimal cycles for the general problem. We also compare these with the Curzon-Ahlborn (CA) efficiency $\eta_{\mathrm{CA}} = 1 - \sqrt{T_c/T_h}$, and note the curious crossover between $\eta^*(\mathcal{T})$ for the general problem and η_{CA}. Moreover, we observe that the optimal cycles obtained in both cases have an asymmetric relation between the corresponding values of τ_1 and τ_2. While there is no *a priori* reason to expect a symmetric partitioning, namely one where $\tau_1 = \tau_2 = \mathcal{T}/2$, similar results were obtained for a heat engine using a quantum dot in Ref. [34] where the efficiencies at maximum power were found to exceed the Curzon-Ahlborn value. The Curzon-Ahlborn efficiency [35,36] was derived for a specific model of heat transfer—it is not a universal bound. However, as discussed in Ref. [31], η_{CA} is close to the efficiency at maximum power for many different models. Further discussion on the topic is beyond the scope of this paper, and we refer the interested reader to the aforementioned review. Our view is that the problem of maximizing power is very system-

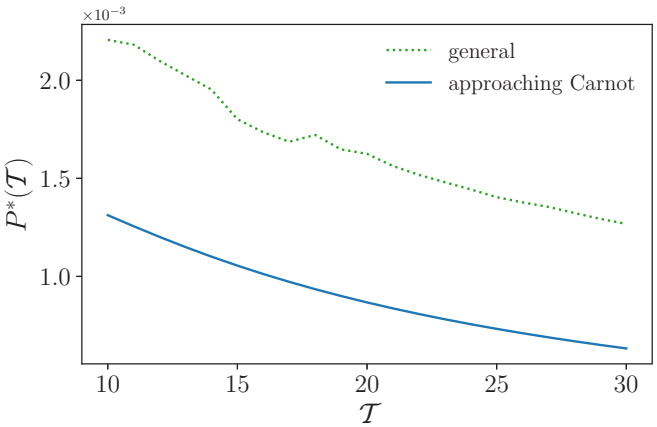


FIG. 9. Comparing maximum power output for optimal cycles obtained in Secs. V B 1 and V B 2. On the y-axis we have the efficiency at maximum power $P^*(\mathcal{T})$. On the x-axis we have the time period of the finite-time cycles, $\mathcal{T}$. We use parameters $T_h = 2$, $T_c = 1$, $\eta_C = 0.5$.

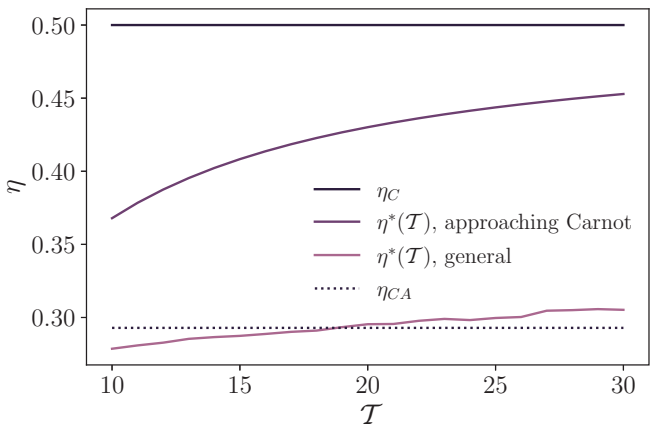


FIG. 10. Comparing efficiency at maximum power for optimal cycles obtained in Secs. V B 1 and V B 2. On the x-axis we have the time period of the finite-time cycles, $\mathcal{T}$. On the y-axis we have efficiency η. We use parameters $T_h = 2$, $T_c = 1$, $\eta_C = 0.5$, and $\eta_{CA} = 0.293$.

specific and depends upon the given setup. To ask for universal bounds on the same requires establishing general features in the model. An attempt along the same direction was made in Ref. [37], where the authors studied a low-dissipation Carnot engine, i.e., one that was operating for a large but finite time period and obtained bounds on the efficiency at maximum power by maximizing power over the thermalization times with the hot and cold reservoirs. (Our problems as studied in Secs. V B 1 and V B 2 are different since we only optimize over one of the two thermalization times.) They were then able to obtain the Curzon-Ahlborn efficiency as a special case when the dissipation with respect to the reservoirs was symmetric. Further generalizations to the bounds obtained in Ref. [37] and related work can be found in Refs. [38,39].

VI. SUMMARY AND OUTLOOK

In this work, we analyzed fluctuations of work done during finite-time processes in two-level systems. We obtained analytic expressions for (a) average work and (b) lower bound for variance as functions of time. We also studied these processes in the context of thermodynamic work extraction cycles performing numerical optimizations for the power output of such cyclic processes. We conclude that finite-time processes are inherently prone to fluctuations that result in broad distributions of work.

Furthermore, we note that since the Markov process that lies at the heart of the overall physical model is not a simple one, an expression for the variance of work could not be obtained. To illustrate this point, we recall Fig. 2. It is clear from that figure that one can write the variance for a discrete L-step process as

$$\sigma_W^2 = \sum_x p(x)W^2(x) - \left(\sum_x p(x)W(x)\right)^2, \qquad (67)$$

where x counts all the paths that correspond to a fixed amount of work $W(x)$, and $p(x)$ is the total probability of occurrence

of those paths during the process. For example, there would be various paths corresponding to $W = \epsilon/2$, and one needs to count these paths and sum their contribution, which is where the complexity lies. However, there is exactly one path each corresponding to $W = 0$ and $W = \epsilon$, respectively. We were able to use this fact to obtain the lower bound for variance. In fact, a similar reasoning was used by the authors of Ref. [23] to derive the distribution of work for a similar process in the limit of slow driving, which allowed them to ignore all but a few relevant paths. On this note, we would like to mention that there exist approaches [40,41] for deriving the distribution of work within the Lindblad master equation formalism for arbitrarily driven quantum systems interacting weakly with the bath. However, such analyses lead to generic expressions for average work and variance. Whether they can be solved to obtain closed-form analytical expressions given specific driving rates and fixed thermalization times is beyond the scope of this work and constitutes a future study. We conclude by stating that one of the original motivations for this work was to observe the resource resonance phenomenon as seen in Ref. [42] (within the resource theory for thermodynamics) in a physical system, but we could not make any relevant connections.

ACKNOWLEDGMENTS

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APPENDIX A: QUANTUM ISOTHERMAL PROCESSES

In the following lemma, we denote the change in the energy of a system during a thermodynamic process $a \mapsto b$ by ΔU_{ab}, we denote the heat exchanged by Q_{ab}, and we denote the work done by W_{ab}.

Lemma 5. A quantum isothermal expansion is such that the gaps between the energy levels of the Hamiltonian H are scaled by a factor $k < 1$.

Proof. A priori, there is nothing constraining the value of k other than the trivial requirement of $k > 0$. However, it is clear that if we choose $k > 1$, then we are stretching the energy levels apart, while if $k < 1$, then we are compressing them together. For an isothermal process $(a \mapsto b)$ to be an expansion, the following should be true:

$$Q_{ab} > 0 \iff \Delta U_{ab} > W_{ab}.$$

We know that $W_{ab} = \Delta F_{ab} = T_h \ln(Z_a/Z_b)$ [11], where $Z_a = \sum_i e^{-\epsilon_i/T_h}$ and $Z_b = \sum_i e^{-k\epsilon_i/T_h}$. Therefore, the following inequality must be satisfied by any quantum isothermal expansion:

$$\sum_j \epsilon_j \left(k \frac{e^{-k\epsilon_j/T_h}}{Z_b} - \frac{e^{-\epsilon_j/T_h}}{Z_a} \right) > T_h(\ln Z_a - \ln Z_b). \tag{A1}$$

Let us assume that $k > 1$. Then

$$e^{-k\epsilon_i/T_h} < e^{-\epsilon_i/T_h} \tag{A2}$$

$$\Rightarrow Z_b < Z_a. \tag{A3}$$

Thus, (A1) implies

$$\sum_j \epsilon_j \left(k \frac{e^{-k\epsilon_j/T_h}}{Z_b} - \frac{e^{-\epsilon_j/T_h}}{Z_a} \right) > 0,$$

which implies

$$k \frac{e^{-k\epsilon_j/T_h}}{Z_b} > \frac{e^{-\epsilon_j/T_h}}{Z_a}. \tag{A4}$$

Now, (A3) implies

$$\frac{e^{-k\epsilon_i/T_h}}{Z_b} > \frac{e^{-k\epsilon_i/T_h}}{Z_a}, \tag{A5}$$

but, by (A2), one has

$$\frac{e^{-\epsilon_i/T_h}}{Z_b} > \frac{e^{-k\epsilon_i/T_h}}{Z_b}. \tag{A6}$$

Combining (A5) with (A6), we have

$$\frac{e^{-\epsilon_i/T_h}}{Z_b} > \frac{e^{-k\epsilon_i/T_h}}{Z_a}. \tag{A7}$$

Differentiating both sides with respect to ϵ_i, we obtain

$$\frac{e^{-\epsilon_i/T_h}}{Z_b} < \frac{k e^{-k\epsilon_i/T_h}}{Z_a}.$$

But, this contradicts (A4). So, the assumption is wrong, which implies that $k < 1$ for a quantum isothermal expansion.

APPENDIX B: ASIDE ON SPECIAL FUNCTIONS

Definition B.1 (Hypergeometric function in integral form).

$$\int dx \frac{e^{px}}{1 + e^{(q-rx)}} = \frac{e^{(p+r)x+q}}{p+r} \times {}_2F_1\left(1, \frac{p}{r} + 1, \frac{p}{r} + 2; -e^{-(q-rx)}\right), \tag{B1}$$

where p, q, and r are rationals, and the hypergeometric function is

$${}_2F_1 : (a, b, c, z) \mapsto \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{z^n}{n!}, \quad |z| \leqslant 1, \tag{B2}$$

and $(x)_n$ denotes the *rising factorial*

$$(x)_n = \begin{cases} 1, & n = 0, \\ x(x+1)\cdots(x+n-1), & n > 0. \end{cases} \tag{B3}$$

Definition B.2 (Lerch transcendent).

$$\Phi_L : (z, s, a) \mapsto \sum_{n=0}^{\infty} \frac{z^n}{(n+a)^s}, \tag{B4}$$

where $z \in \mathbb{C}$ and $\mathrm{Re}(a) > 0$. We can then write the function $\mathcal{G}$ (Definition 1) in terms of the Lerch transcendent as

$$\mathcal{G}(t) = \frac{\kappa\tau T_h}{\epsilon} e^{-\delta(t)/T_h}\, \Phi_L\Big(-e^{-\delta(t)/T_h}, 1, \frac{\kappa\tau T_h}{\epsilon} + 1\Big). \tag{B5}$$

APPENDIX C: PROOF OF LEMMA 3

Proof. W_{ab} and W_{cd} are essentially deterministic and are given by (55) and (58), while W_{bc} and W_{da} are random variables. In Table I, we list all the possible states that the system could be in at each of the four nodes *a, b, c, d*, and thus we obtain all the possible values for $W_{bc} - W_{da}$. Thus, we can obtain an expression for the average work done by simply multiplying and adding the corresponding entries of columns W_C and $\Pr(W_C)$ to arrive at

$$\begin{aligned}\mu_{W_C} &= (T_h - T_c)\ln\frac{Z(\delta_b)}{Z(\delta_a)} - \left(1 - \frac{T_c}{T_h}\right)\delta_a p_a \\ &\quad + \left(1 - \frac{T_c}{T_h}\right)\delta_b p_b \\ &= (T_h - T_c)\ln\frac{Z(\delta_b)}{Z(\delta_a)} - \left(1 - \frac{T_c}{T_h}\right)(\delta_a p_a - \delta_b p_b) \\ &= \left(1 - \frac{T_c}{T_h}\right)\left(T_h \ln\frac{Z(\delta_b)}{Z(\delta_a)} + \delta_b p_b - \delta_a p_a\right).\end{aligned} \tag{C1}$$

We can then derive the average Carnot efficiency η_C^{avg} by dividing the average work done by the heat input (which is when the system undergoes isothermal expansion from point *a* to *b*), Q_{ab}. The heat exchanged during a process, denoted by Q, is given by the First Law of Thermodynamics, i.e., $Q = \Delta U - W$, where ΔU is the change in the total energy of the system during the process, while W is the corresponding work yield/cost. In our case, the process is an isothermal expansion $a \mapsto b$, so $\Delta U_{ab} = (\delta_b p_b - \delta_a p_a)$ and $W = -W_{ab}$, where W_{ab} is the deterministic work yield of the process and is given by (55). Thus, we have

$$Q_{ab} = (\delta_b p_b - \delta_a p_a) + T_h \ln\frac{Z(\delta_b)}{Z(\delta_a)}. \tag{C2}$$

Since efficiency is defined as the ratio of the work output and the heat input, (C1) and (C2) imply (62).

TABLE I. Occupation of the ground state is designated by 0 and that of the excited state by 1. The Carnot cycle is $a \mapsto b \mapsto c \mapsto d \mapsto a$. Starting at a with the system in the ground state as one completes the cycle, the system could be in the excited state—it undergoes thermalization from $c \mapsto d$. Same color entries under the $W_{bc} + W_{da}$ column are identical and the probabilities corresponding to those entries add up.

$a\mapsto$	$b\mapsto$	$c\mapsto$	$d\mapsto$	a	$W_{bc} - W_{da}$	$\Pr(W_{bc} - W_{da})$
0	0	0	0	0	0	$(1-p_a)^2(1-p_b)$
0	0	0	1	1	$-(\delta_a - \delta_d)$	$(1-p_a)(1-p_b)p_a$
0	1	1	0	0	$\delta_b - \delta_c$	$(1-p_a)^2 p_b$
0	1	1	1	1	$\delta_b - \delta_c - \delta_a + \delta_d$	$(1-p_a)p_b p_a$
1	0	0	0	0	0	$p_a(1-p_a)(1-p_b)$
1	0	0	1	1	$-(\delta_a - \delta_d)$	$p_a^2(1-p_b)$
1	1	1	0	0	$\delta_b - \delta_c$	$p_a p_b(1-p_a)$
1	1	1	1	1	$\delta_b - \delta_c - \delta_a + \delta_d$	$p_a^2 p_b$

APPENDIX D: PROOF OF LEMMA 4

Proof. Note that the points *a*, *b*, *c*, and *d* as in Fig. 5, defining a cycle of a Carnot engine, are not independent—see (56) and (59). Thus, there are only two free variables that define any particular cycle. Let us set δ_a and δ_c as the independent ones. Then, changing variables in (C1) and plugging the expressions for the partition function Z, p_a, and p_b, we obtain

$$\begin{aligned}\mu_{W_C}(\delta_a,\ \delta_c) = (T_h - T_c)\Bigg(&\ln\left(\frac{1 + e^{-\delta_a/T_h}}{1 + e^{-\delta_c/T_c}}\right) \\ &+ \frac{\delta_a/T_h}{1 + e^{\delta_a/T_h}} - \frac{\delta_c/T_c}{1 + e^{\delta_c/T_c}}\Bigg).\end{aligned} \tag{D1}$$

Introducing $x := \delta_a/T_h$ and $y := \delta_c/T_c$ reduces the equation above to

$$\mu_{W_C}(x,\ y) = (T_h - T_c)\left(\ln\left(\frac{1 + e^{-x}}{1 + e^{-y}}\right) + \frac{x}{1 + e^{x}} - \frac{y}{1 + e^{y}}\right). \tag{D2}$$

Let us now look at the function

$$f : x \mapsto (1 + e^{-x})\, e^{\frac{x}{1+e^x}}. \tag{D3}$$

Evaluating the derivative of this function, we obtain

$$f'(x) = -\left(\frac{x}{1 + e^x}\right) e^{\frac{x}{1+e^x}} < 0, \quad \forall\, x > 0. \tag{D4}$$

This means that f is a monotonically decreasing function on $\mathbb{R}^+$. Hence, the minimum/maximum would be attained on the boundaries of the interval $\mathcal{I} \subset \mathbb{R}^+$. Note that (D2) can be written in terms of f simply as

$$\mu_{W_C}(x,\ y) = (T_h - T_c)(\ln\ f(x) - \ln\ f(y)). \tag{D5}$$

As ln is a monotonically increasing function, $\ln \circ f$ would thus be monotonically decreasing since f is monotonically decreasing. Now, as $\mu_{W_C} < 0$, where the negative sign implies work output, maximizing the average work output amounts to minimizing μ_{W_C} with respect to x and y. So, we have

$$\begin{aligned}&\min_{x,\ y\in\mathcal{I}} \mu_{W_C}(x,\ y) \\ &\quad = \min_{x,\ y\in\mathcal{I}} (T_h - T_c)(\ln\ f(x) - \ln\ f(y)) &\text{(D6)}\\ &\quad = (T_h - T_c)\Big(\min_{x\in\mathcal{I}} \ln\ f(x) - \max_{y\in\mathcal{I}} \ln\ f(y)\Big). &\text{(D7)}\end{aligned}$$

As $\ln \circ f$ is monotonically decreasing, it implies that

$$\begin{aligned}\min_{x,\ y\in\mathcal{I}} \mu_{W_C}(x,\ y) = (T_h - T_c)\Big(&\ln\ f\Big(\max_{x\in\mathcal{I}} x\Big) \\ &- \ln\ f\Big(\min_{y\in\mathcal{I}} y\Big)\Big).\end{aligned} \tag{D8}$$

Substituting for x and y in terms of δ_a and δ_c and noting that

$$\max_{\delta_a} \delta_a = \delta_{\max} \quad \text{and} \quad \min_{\delta_c} \delta_c = \delta_{\min} \tag{D9}$$

gives us

$$\arg\max_{\delta_a,\ \delta_c} \mu_{W_C}(\delta_a, \delta_c) = (\delta_{\max},\ \delta_{\min}). \tag{D10}$$

APPENDIX E: PARTIAL THERMALIZATION UNDER ASSUMPTION 1 WHILE INCREASING THE ENERGY GAP

Definition E.1. Given the energy gap $\delta(t)$ of a two-level system at time $t < \tau$, we define the function

$$\mathcal{H} : t \mapsto \sum_{n=0}^{\infty} \frac{\left(e^{-\frac{\delta(t)}{T_c}}\right)^n}{\left(\frac{n\epsilon}{\kappa\tau T_c} + 1\right)}, \tag{E1}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$, κ is the thermalization rate, and T_c is the temperature of the ambient bath.

The function $\mathcal{H}$ is a monotone function in t. For δ monotonically increasing in t, $\mathcal{H}$ monotonically decreases. This follows by noting that $e^{-\delta}$ is also monotonically decreasing in t.

Lemma 6 (Time evolution of occupation probabilities under partial thermalization while increasing the energy gap). Given a two-level system that undergoes partial thermalization as per Assumption 1 in the presence of a bath at temperature T_c for a time τ such that its energy gap changes from $\delta_{\min}$ to $\delta_{\max}$, the probability of the system to be in the excited state at any time $0 < t < \tau$ is

$$p(t) = p_0 e^{-\kappa t} + \mathcal{H}(t) - e^{-\kappa t}\mathcal{H}(0), \tag{E2}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$, $p_0 = p(0)$, and $\delta(t) = \delta_{\min} + \epsilon t/\tau$.

Proof. Rewriting the differential equation for general partial thermalization processes where the hot bath is replaced by the cold bath in (2), we have

$$\frac{dp}{dt} + \kappa p(t) = \kappa \gamma_c(\delta(t)), \tag{E3}$$

which can be integrated along with the initial condition $p(0) = p_0$ to obtain

$$p(t) = p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \int_0^t e^{\kappa t'} \gamma_c(\delta(t'))\, dt'. \tag{E4}$$

Given Assumption 1 and the boundary conditions $\delta(0) = \delta_{\min}$ and $\delta(\tau) = \delta_{\max}$, we have

$$\delta(t) = \delta_{\min} + \frac{\epsilon}{\tau} t, \tag{E5}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$. Plugging $\gamma_c(\delta(t)) = \frac{1}{1+e^{\delta(t)/T_c}}$ and (E5) in (E4), we obtain

$$p(t) = p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \int_0^t \frac{e^{\kappa t'}}{1 + e^{\frac{(\delta_{\min} + \epsilon t'/\tau)}{T_c}}}\, dt'. \tag{E6}$$

Evaluating the integral above, we obtain

$$\begin{aligned}
p(t) &= p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \left\{ \frac{e^{\kappa t'}}{\kappa}\, {}_2F_1\left(1, \frac{\kappa\tau T_c}{\epsilon}, \frac{\kappa\tau T_c}{\epsilon} + 1; -e^{\frac{(\delta_{\min} + \epsilon t'/\tau)}{T_c}}\right)\Bigg|_0^t \right\} \\
&= p_0 e^{-\kappa t} + \kappa e^{-\kappa t} \left\{ \frac{e^{\kappa t}}{\kappa}\, {}_2F_1\left(1, \frac{\kappa\tau T_c}{\epsilon}, \frac{\kappa\tau T_c}{\epsilon} + 1; -e^{\frac{\delta(t)}{T_c}}\right) - \frac{1}{\kappa}\, {}_2F_1\left(1, \frac{\kappa\tau T_c}{\epsilon}, \frac{\kappa\tau T_c}{\epsilon} + 1; -e^{\frac{\delta_{\min}}{T_c}}\right) \right\} \\
&= p_0 e^{-\kappa t} + {}_2F_1\left(1, \frac{\kappa\tau T_c}{\epsilon}, \frac{\kappa\tau T_c}{\epsilon} + 1; -e^{\frac{\delta(t)}{T_c}}\right) - e^{-\kappa t}\, {}_2F_1\left(1, \frac{\kappa\tau T_c}{\epsilon}, \frac{\kappa\tau T_c}{\epsilon} + 1; -e^{\frac{\delta_{\min}}{T_c}}\right).
\end{aligned} \tag{E7}$$

Next, using Definition 1 we can write

$$\begin{aligned}
{}_2F_1(1, a, 1 + a; -z) &= \sum_{n=0}^{\infty} \frac{n!(a)_n}{(1+a)_n} \frac{(-z)^n}{n!} \\
&= \sum_{n=0}^{\infty} \frac{(a)(1+a)\cdots(n-1+a)}{(1+a)(2+a)\cdots(n+a)} (-z)^n \\
&= \sum_{n=0}^{\infty} \frac{a\,(-z)^n}{(n+a)} \\
&= \sum_{n=0}^{\infty} \frac{(-z)^n}{\left(\frac{n}{a} + 1\right)}.
\end{aligned} \tag{E8}$$

Using (E8) we can write (E7) in terms of $\mathcal{H}$ to obtain (E2).

Lemma 7 (Average work when increasing the energy gap). The average work done by a two-level system during a process as per Assumption 1 along with partial thermalizations in the presence of a bath at temperature T_h for a time τ such that its energy gap changes from $\delta_{\min}$ to $\delta_{\max}$ is

$$\mu_W(\tau) = -W_{\text{iso}}^{T_c} - \frac{W_{\text{ad}}}{\kappa\tau}(1 - e^{-\kappa\tau}) + \frac{\epsilon}{\kappa\tau}\{\mathcal{H}(\tau) - e^{-\kappa\tau}\mathcal{H}(0)\}, \tag{E9}$$

where $\epsilon = \delta_{\max} - \delta_{\min}$, $p_0 = p(0)$, and $W_{\text{iso}}^{T_c}$ is the work output of the corresponding isothermal process, i.e., $W_{\text{iso}}^{T_c} = -T_c \ln \frac{Z(\delta_{\min})}{Z(\delta_{\max})}$, where Z is the partition function $Z : \delta \mapsto 1 + e^{-\delta/T_c}$.

Proof. We start by noting that

$$\frac{dp}{d\delta} = \frac{dp}{dt}\frac{dt}{d\delta} = -\frac{\kappa\tau}{\epsilon}(\gamma_h(\delta) - p), \tag{E10}$$

where the last line follows from (2) and Assumption 1 while suppressing the dependence on t. Integrating (18) with respect to δ from $\delta_{\min}$ to $\delta_{\max}$, we have

$$\int_{\delta_{\min}}^{\delta_{\max}} p\, d\delta = \int_{\delta_{\min}}^{\delta_{\max}} \gamma_c(\delta) d\delta + \frac{\epsilon}{\kappa\tau} \int_{\delta_{\min}}^{\delta_{\max}} \frac{dp}{d\delta} d\delta. \tag{E11}$$

Thus, (8) and (E11) together imply

$$\mu_W(\tau) = \int_{\delta_{\min}}^{\delta_{\max}} \gamma_c(\delta) d\delta + \frac{\epsilon}{\kappa\tau} \int_{\delta_{\min}}^{\delta_{\max}} \frac{dp}{d\delta} d\delta. \quad \text{(E12)}$$

The first term on the right-hand side is the negative of the work done during the corresponding isothermal process (when the energy gap changes from $\delta_{\max}$ to $\delta_{\min}$). Substituting the expression for $\gamma_c(\delta)$ and evaluating the integral gives us the first term of (E12) as

$$\int_{\delta_{\min}}^{\delta_{\max}} \gamma_c(\delta) d\delta = T_c \ln \frac{Z(\delta_{\min})}{Z(\delta_{\max})} = -W_{\text{iso}}^{T_c}, \quad \text{(E13)}$$

where Z is the partition function $Z : \delta \mapsto 1 + e^{-\delta/T_c}$. Next, we evaluate the integral in the second term in (E12) using Lemma 6. First we note that

$$\int_{\delta_{\min}}^{\delta_{\max}} \frac{dp}{d\delta} d\delta = p(\delta_{\max}) - p(\delta_{\min}).$$

As $p(\delta_{\min}) = p(0) = p_0$ is given and $p(\delta_{\max}) = p(\tau)$, we use (E2) to obtain

$$p(\delta_{\max}) - p(\delta_{\min}) = -p_0(1 - e^{-\kappa\tau}) + \mathcal{H}(\tau) - e^{-\kappa\tau}\mathcal{H}(0). \quad \text{(E14)}$$

Plugging (E13) and (E14) in (E12) along with (24), we obtain (E9).

[1] H. B. Callen, *Thermodynamics & an Introduction to Thermostatistics* (Wiley, New York, 2006).
[2] C. Jarzynski, Annu. Rev. Condens. Matter Phys. **2**, 329 (2011).
[3] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[4] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
[5] C. M. Dobson, Nature (London) **426**, 884 (2003).
[6] A. Alemany and F. Ritort, Europhys. News **41**, 27 (2010).
[7] C. Bustamante, J. Liphardt, and F. Ritort, Phys. Today **58**(7), 43 (2005).
[8] A. B. Kolomeisky and M. E. Fisher, Annu. Rev. Phys. Chem. **58**, 675 (2007).
[9] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, and C. Bustamante, Science **296**, 1832 (2002).
[10] A. J. P. Garner, *Thermodynamics in the Quantum Regime* (Springer, Cham, 2018), p. 651.
[11] J. Åberg, Nat. Commun. **4**, 1925 (2013).
[12] O. C. O. Dahlsten, R. Renner, E. Rieper, and V. Vedral, New J. Phys. **13**, 053015 (2011).
[13] L. Del Rio, J. Åberg, R. Renner, O. Dahlsten, and V. Vedral, Nature (London) **474**, 61 (2011).
[14] P. Faist, F. Dupuis, J. Oppenheim, and R. Renner, Nat. Commun. **6**, 7669 (2015).
[15] M. Tomamichel, *Quantum Information Processing with Finite Resources: Mathematical Foundations* (Springer, 2015), Vol. 5.
[16] A. Rényi, in *Proceedings of the Fourth Berkeley Symposium on Mathematical Statistics and Probability, Volume 1: Contributions to the Theory of Statistics* (University of California Press, 1961).
[17] R. Renner and S. Wolf, in *Proceedings of International Symposium on Information Theory, Chicago, IL, USA* (IEEE, Piscataway, NJ, 2004), p. 233.
[18] R. Renner, Ph.D. thesis, ETH Zurich, 2005.
[19] M. Ziman, P. Štelmachovič, and V. Bužek, Open Syst. Inf. Dyn. **12**, 81 (2005).
[20] V. Scarani, M. Ziman, P. Štelmachovič, N. Gisin, and V. Bužek, Phys. Rev. Lett. **88**, 097905 (2002).
[21] F. Ciccarello, Quantum Meas. Quantum Metrology **4**, 53 (2017).
[22] Y.-H. Ma, D. Xu, H. Dong, and C.-P. Sun, Phys. Rev. E **98**, 022133 (2018).
[23] R. Marathe and A. Dhar, Phys. Rev. E **72**, 066112 (2005).
[24] E. Bäumer, M. Perarnau-Llobet, P. Kammerlander, H. Wilming, and R. Renner, Quantum **3**, 153 (2019).
[25] T. A. Brun, Am. J. Phys. **70**, 719 (2002).
[26] O. Tange, *GNU Parallel 2018* (Lulu.com, 2018).
[27] H. J. D. Miller, M. Scandi, J. Anders, and M. Perarnau-Llobet, Phys. Rev. Lett. **123**, 230603 (2019).
[28] M. Scandi, H. J. D. Miller, J. Anders, and M. Perarnau-Llobet, Phys. Rev. Research **2**, 023377 (2020).
[29] H. T. Quan, Y.-X. Liu, C. P. Sun, and F. Nori, Phys. Rev. E **76**, 031105 (2007).
[30] This means that if the system was in the ground state, then it continues to be in the ground state of the new Hamiltonian.
[31] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).
[32] Wolfram Research, Inc., "Mathematica, Version 12.1," Champaign, IL, 2020.
[33] Wolfram Language & System Documentation Center, "Constrained optimization".
[34] P. E. Harunari, F. S. Filho, C. E. Fiore, and A. Rosas, arXiv:2012.09296.
[35] F. L. Curzon and B. Ahlborn, Am. J. Phys. **43**, 22 (1975).
[36] I. Novikov, J. Nucl. Energy (1954) **7**, 125 (1958).
[37] M. Esposito, R. Kawai, K. Lindenberg, and C. Van den Broeck, Phys. Rev. Lett. **105**, 150603 (2010).
[38] V. Holubec and A. Ryabov, J. Stat. Mech.: Theor. Exp. (2016) 073204.
[39] Y.-H. Ma, D. Xu, H. Dong, and C.-P. Sun, Phys. Rev. E **98**, 042112 (2018).
[40] H. J. D. Miller, M. H. Mohammady, M. Perarnau-Llobet, and G. Guarnieri, arXiv:2011.11589.
[41] M. Silaev, T. T. Heikkilä, and P. Virtanen, Phys. Rev. E **90**, 022103 (2014).
[42] K. Korzekwa, C. T. Chubb, and M. Tomamichel, Phys. Rev. Lett. **122**, 110403 (2019).