

Heat engines with single-shot deterministic work extractionFederico Cerisola,^{1,2,3,*} Facundo Sapienza^{4,†} and Augusto J. Roncaglia^{1,2,‡}¹*Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Física, Buenos Aires, Argentina*²*CONICET - Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Buenos Aires, Argentina*³*Department of Materials, University of Oxford, Oxford OX1 3PH, United Kingdom*⁴*Department of Statistics, University of California, Berkeley, 367 Evans Hall, Berkeley, California 94720, USA*

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We introduce heat engines working in the nanoregime that allow one to extract a finite amount of deterministic work. Using the resource theory approach to thermodynamics, we show that the efficiency of these cycles is strictly smaller than Carnot's, and we associate this difference with a fundamental irreversibility that is present in single-shot transformations. When fluctuations in the extracted work are allowed there is a trade-off between their size and the efficiency. As the size of fluctuations increases so does the efficiency and optimal efficiency is attained for unbounded fluctuations, while a certain amount of deterministic work is drawn from the cycle. Finally, we show that when the working medium is composed of many particles, by creating an amount of correlations between the subsystems that scale logarithmically with their number, Carnot's efficiency can also be approached in the asymptotic limit along with deterministic work extraction.

DOI: [10.1103/PhysRevE.106.034135](https://doi.org/10.1103/PhysRevE.106.034135)**I. INTRODUCTION**

Since its formulation, thermodynamics has become one of the cornerstones of physics. Originally motivated by the study of macroscopic thermal machines like steam engines, it has now been pushed well outside its original scope into the limit of a small number of systems in the quantum realm [1–3]. Pursuing the identification of the limitations and advantages of these devices that operates in the nanoregime, an extensive deal of work has been devoted to the study for instance of cycles analogous to Carnot's [4–11] or Otto's [12–17], the performance of quantum refrigerators [18–21], heat engines that exploit the quantumness nonclassical reservoirs [22–24], or quantum measurements [25–29]. Like in the standard scenario, most of these analyses were focused on the study of average work extraction. This assumption is well justified in the macroscopic limit due to the fact that the amount of fluctuations decreases with the number of particles. However, in small systems work fluctuations dominate and may be even greater than the mean value of work. Therefore, it becomes relevant to understand limitations of heat engines in single realizations with controlled, or bounded, fluctuations of work in this regime.

Among the different approaches that have been developed to characterize single-shot thermodynamic transformations of nanoscale systems in contact with a thermal bath, a recent framework that gained a lot of interest is the so-called resource theory of thermodynamics [30–51]. Within this framework, a detailed account of every energy exchange between system and heat bath imposes severe restrictions to the allowed thermodynamic transformations that go beyond the standard

second law [31–34]. In fact, this set of restrictions determines that, in general, the minimum amount of deterministic work yielded in a given transformation is greater than the maximum work that can be drawn from the reverse process [31–34]. Remarkably, the emergence of this fundamental notion of irreversibility is absent in the standard scenario, where the free energy difference determines both the work that can be extracted from a given transformation and the work that needs to be invested to generate it. Thus, naturally, one expects poorer performance for heat engines working in such a regime. However, the existing results seem to suggest that it is not even possible to design a cycle able to extract a finite amount of deterministic work in the single-shot regime [31,39,52,53].

Here we show that in fact one can define such heat engines in the single-shot regime. We introduce thermodynamic cycles that allow one to extract a deterministic amount of work from a nanoscale system (working medium) in contact with two thermal baths. These cycles can be described in two ways: either in terms of the collection of equilibrium states that the working medium reaches at the end of each stroke when it is subjected to a driving or in terms of a set of nonequilibrium states through which the working medium passes after the different strokes with fixed Hamiltonian. We show that the efficiency of these engines is strictly smaller than Carnot for deterministic work extraction. These two types of engines also allow us to analyze the influence of fluctuations of work and the size of the working medium on the efficiency. Indeed, we show that the efficiency of these engines can be enhanced either by allowing fluctuation in the extracted work or by increasing the size of the working medium.

II. SINGLE-SHOT SCENARIO

Let us start by setting up the scenario we will consider. The fundamental components of an ordinary heat engine are two thermal baths at different temperatures T_{hot} and T_{cold} (with

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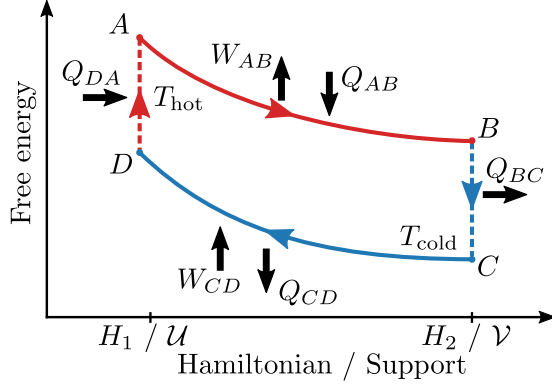


FIG. 1. Pictorial representation of thermodynamic cycles for deterministic work extraction. For the cycles connecting equilibrium states, the transformations $A \rightarrow B$ or $C \rightarrow D$ are defined through the initial and final Hamiltonians. For the engines operating between nonequilibrium states, the states at A and B are identified by the support on the energy eigenbasis, which uniquely determines these states. The strokes $A \rightarrow B$ and $C \rightarrow D$ are reversible processes even in the single-shot regime, while the two other strokes involve an irreversible thermalization.

$T_{\text{cold}} < T_{\text{hot}}$) and a working medium \mathcal{S} that undergoes a cyclic transformation. We assume that the working medium is an arbitrary finite dimensional quantum system and we have at our disposal two infinite heat baths in thermal states τ_B . Work will be quantified by considering an additional degree of freedom that acts as a battery [32,33]. The battery is modeled as quantum system \mathcal{W} with its own Hamiltonian $H_{\mathcal{W}}$ that, in a deterministic (fluctuation free) transformation, starts and ends up in a pure energy eigenstate of $H_{\mathcal{W}}$. Thus, if the initial state of the battery is an eigenstate with energy E_1 , and after a given transformation it ends up in an eigenstate with energy E_2 , we will then say that an amount of deterministic work $W = E_2 - E_1$ (if $E_2 > E_1$) has been drawn or it has been yielded (if $E_2 < E_1$) in the transformation. For deterministic work extraction, a two-level system will be enough.

The cycles we will introduce can be described by a four stroke process as depicted in Fig. 1. At the beginning of each cycle the system, battery, and baths start uncorrelated in a product state, and during each stroke the system interacts with only one of the baths. As we are interested in work extraction in small systems we will take into account all sources of energy transfer [32–34]. Thus we also assume that during each stroke the components interact through an energy-preserving unitary transformation U , such that $[U, H_{\mathcal{S}} + H_{\mathcal{W}} + H_{\mathcal{B}}] = 0$, where $H_{\mathcal{S}}$ is the Hamiltonian of the system \mathcal{S} and $H_{\mathcal{B}}$ is the Hamiltonian of the corresponding bath \mathcal{B} . This is a strict energy conservation requirement, analogous to the first law, and ensures that the unitary transformation is not injecting energy. Thus all energy exchanges with the battery come from the bath and/or the system (working medium). In this way, an initial state η (system + battery) can be transformed into a final one σ after tracing over the degrees of freedom of the bath: $\sigma = \text{tr}_{\mathcal{B}}[U(\eta \otimes \tau_{\mathcal{B}})U^\dagger]$; this is called a *thermal transformation* and will be denoted as $\eta \rightarrow \sigma$ [33,34].

In this way, we can generically describe each stroke by a thermal transformation. Let us consider a finite dimensional system with Hamiltonian $H_{\mathcal{S}} = \sum_E E \Pi_E$, where Π_E are projectors over the energy subspace E , in an initial block-diagonal state $\rho = \sum_{E,g} \lambda_{E,g} |E, g\rangle \langle E, g|$ (g accounts for the degeneracy of the energy levels). Then, the maximum amount of deterministic work W_{ext} that can be extracted in contact with a reservoir at temperature T is given by

$$W_{\text{ext}}(\rho) = F_0(\rho) - F(\tau_{\mathcal{S}}), \quad (1)$$

where $F_0(\rho) = -\beta^{-1} \ln \sum_{E \in \text{supp}(\rho)} e^{-\beta E}$, $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant, $\text{supp}(\rho)$ is the support of the state ρ , and $F(\tau_{\mathcal{S}}) = -\beta^{-1} \ln Z_{\mathcal{S}}$ is the standard free energy of the thermal state $\tau_{\mathcal{S}} = e^{-\beta H_{\mathcal{S}}} / Z_{\mathcal{S}}$. This is called the *extractable work* and is obtained by maximizing W over the thermal transformation $\rho \otimes |0\rangle \langle 0|_{\mathcal{W}} \rightarrow \tau_{\mathcal{S}} \otimes |W\rangle \langle W|_{\mathcal{W}}$, with $H_{\mathcal{W}} = W|W\rangle \langle W|_{\mathcal{W}}$. Notice that, to be able to extract a nonzero deterministic amount of work, the state cannot have full support in the energy eigenbasis. The inverse transformation, where a nonequilibrium state ρ is created out of an initial thermal state, requires a minimum amount of deterministic work

$$W_{\text{form}}(\rho) = F_{\infty}(\rho) - F(\tau_{\mathcal{S}}), \quad (2)$$

where $F_{\infty} = \beta^{-1} \ln \max_{E,g} \{\lambda_{E,g} e^{\beta E}\}$; this is the so-called *work of formation*. Remarkably, $W_{\text{form}}(\rho) \geq W_{\text{ext}}(\rho)$ and the inequality is strict except for very specific cases that we will discuss later. This reflects a fundamental irreversibility that exists in the single-shot regime [33,34]. Under all these assumptions, in the following we will present a set of microscopic heat engines that allow deterministic work extraction.

III. CYCLES IN TERMS OF EQUILIBRIUM STATES

As it is usual in standard thermodynamics we will start by defining cycles in terms of thermal states of the working medium. In this way, one can notice from Eq. (1) that a stroke where the working medium starts in a thermal state is useless for deterministic work extraction if the Hamiltonian is constant during the process since, in this case, no deterministic work can be extracted from full rank states. However, we can overcome this issue by introducing a driving, where the Hamiltonian of the working medium changes from H_1 to H_2 . This thermal transformation can be modeled by introducing an auxiliary two-level system \mathcal{C} with trivial Hamiltonian that acts as a *clock* [33,34]. Then, by defining the Hamiltonian of the working medium as $H_{\mathcal{S}\mathcal{C}} = H_1 \otimes |0\rangle \langle 0| + H_2 \otimes |1\rangle \langle 1|$, with $\{|0\rangle, |1\rangle\}$ an orthonormal basis of \mathcal{C} , the above work extraction process can be formally expressed as

$$\tau_{\mathcal{S},1} \otimes |0\rangle \langle 0|_{\mathcal{C}} \otimes |0\rangle \langle 0|_{\mathcal{W}} \rightarrow \tau_{\mathcal{S},2} \otimes |1\rangle \langle 1|_{\mathcal{C}} \otimes |W\rangle \langle W|_{\mathcal{W}}, \quad (3)$$

where $\tau_{\mathcal{S},i}$ is the thermal equilibrium state of \mathcal{S} with Hamiltonian H_i . This type of transformation resembles the classical isothermal transformation of a gas. Thus it is easy to show now that the maximum deterministic work W that can be extracted after this transformation is simply equal to the

standard free energy difference $W = \Delta F = F(\tau_{S,2}) - F(\tau_{S,1})$. Notably, this transformation holds an important property: it is *reversible*, meaning that the amount of work yielded in the inverse transformation is also equal to W .

The four stroke cycles we define below ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$) are illustrated in Fig. 1. At the end of each stroke the system is in a thermal state, so we will label these states as (H, T) , indicating that the system is in equilibrium at temperature T with Hamiltonian H . Let us analyze the cycle in detail; as we said before \mathcal{S} is a general finite dimensional system. Initially, the system starts at A in equilibrium with (H_1, T_{hot}) . The first stroke is such that the system is driven from $H_1 \rightarrow H_2$ in contact with the hot bath and ends up at B in equilibrium with (H_2, T_{hot}) . The extracted work after this step is equal to $\Delta F_{AB} = F_A - F_B$, where $F_{(\cdot)}$ is the standard free energy of the equilibrium state at each point. During the second stroke the system is brought in contact with the cold bath and thermalizes; thus the state of the system at C is (H_2, T_{cold}) . This transformation is achieved at no work cost and an amount of heat Q_{BC} is dissipated in the cold bath. In terms of the resource theory this is a consequence of the fact that the thermal state is *thermomajorized* by all states [33]. In the third stroke, at a work cost equal to $\Delta F_{DC} = F_D - F_C$, the system is driven from $H_1 \rightarrow H_2$, still in contact with cold bath, and ends up at D in a thermal state (H_1, T_{cold}) . Finally, the system is brought again in contact with the hot bath and thermalizes after receiving an amount of heat Q_{DA} , thus reaching the initial state. In summary, after this cycle it is possible to extract a deterministic amount of work equal to

$$W_{\text{cycle}} = F_A - F_B - F_D + F_C. \quad (4)$$

Notably, the derivation is general, as we did not impose any condition on the dimension of the system, Hamiltonians, or temperatures. However, the work W_{cycle} drawn in the cycle of course depends on these details.

Efficiency

The performance of any heat engine is evaluated by computing their efficiency. In order to obtain the efficiency of these cycles, we have to compute the amount of heat exchanged with the baths. If a thermal operation has an associated single-shot deterministic work cost W and the average internal energy change of the system is ΔE , then the heat Q exchanged with the reservoir during the transformation is

$$Q = \Delta E - W. \quad (5)$$

Due to the fact that the state of the system itself has a probabilistic distribution of energy, heat will be a fluctuating quantity; only if the system were in a pure state could we have a definite value of internal energy and therefore of the heat exchanged.

Now, the efficiency is defined as the ratio between the extracted work and the heat exchange with the hot bath:

$$\begin{aligned} \eta &= \frac{W_{\text{cycle}}}{Q_{\text{hot}}} = 1 - \frac{Q_{\text{cold}}}{Q_{\text{hot}}} \\ &= 1 - \frac{T_{\text{cold}}[S_C - S_D] + E_B - E_C}{T_{\text{hot}}[S_B - S_A] + E_A - E_D}, \end{aligned} \quad (6)$$

where $S_{(\cdot)}$ and $E_{(\cdot)}$ are the entropy and average energy of the system in each state, respectively. One can easily check that this value is indeed strictly smaller than Carnot's efficiency,

$$\eta < \eta_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}. \quad (7)$$

As we will see, this is related with the heat exchange during the thermalization processes $B \rightarrow C$ and $D \rightarrow A$, which are irreversible in the single-shot regime. In fact, while the transformation $B \rightarrow C$ can be done without investing work, the inverse transformation $C \rightarrow B$ requires a finite amount of work. This is due to the fact the state at B with H_2 in contact with the hot bath is a nonequilibrium state for the cold bath. Hence one can show that the efficiency can be improved as the heats Q_{DA} and Q_{BC} are reduced. In fact, as $Q_{BC} \rightarrow 0$ and $Q_{DA} \rightarrow 0$, $\eta \rightarrow \eta_{\text{Carnot}}$. This behavior is illustrated in Fig. 2 for a single-qubit heat engine. There, the Hamiltonians at A and B are $H_1 = \hbar\omega_1|1\rangle\langle 1|$ and $H_2 = \hbar\omega_2|1\rangle\langle 1|$, respectively, where $\{|0\rangle, |1\rangle\}$ is an orthonormal basis of \mathcal{S} . In Fig. 2 we can see the efficiency, work, and irreversible heat exchange for this engine; thus for $\hbar\omega_2 \ll k_B T_{\text{cold}}$ and $\hbar\omega_1 \gg k_B T_{\text{hot}}$ the irreversible heat is drastically reduced and Carnot efficiency is approached. This is a consequence of the fact that the irreversible heat dissipated during the thermalization steps (both Q_{BC} and Q_{DA}) is drastically reduced whenever the system gap is much smaller or larger than the temperature of the heat bath [as can be seen in Fig. 2(c)]. This cycle can be considered as a generalization of the Stirling cycle [54], since they share two strokes where work is extracted or yielded in contact with heat baths and two strokes where there is only heat exchange with the baths. The efficiency of the classical Stirling engine can be increased through the interaction with a regenerator that transfers the heat between the isochoric transformations. Since the amount of heat that is absorbed and dissipated in those strokes is equal, the efficiency of the classical cycle could be as high as Carnot's efficiency. As we will see bellow, our cycle is such that, instead of using a regenerator to reach Carnot's efficiency, we can allow fluctuations in the extractable work.

As we said, there is a different way to approach Carnot's efficiency in this cycle. This is at the expense of allowing some fluctuations in the work extraction. Single-shot transformations with bounded fluctuations of work have been thoroughly studied in [39], where it was shown that if arbitrarily large fluctuations are allowed it is possible to extract an average work equal to the free energy difference. In particular, this means that we can also extract some fluctuating work during the thermalization steps (second and fourth), and actually if we allow arbitrary large fluctuations the mean value of this work equals the free energy difference: $\langle W_{BC} \rangle = F_B - F_C$ and $\langle W_{DA} \rangle = F_D - F_A$. It is then straightforward to see that in this limit the efficiency of our cycle is precisely Carnot, $\eta = \eta_{\text{Carnot}}$. Notably, by allowing fluctuations we do not change the deterministic work that is being drawn from $A \rightarrow B$, since over this stroke work is already equal to the free energy difference. However, if the size of fluctuations is bounded, the average work that can be extracted during the thermalization steps is $\langle W \rangle < \Delta F$ and therefore the efficiency increases.

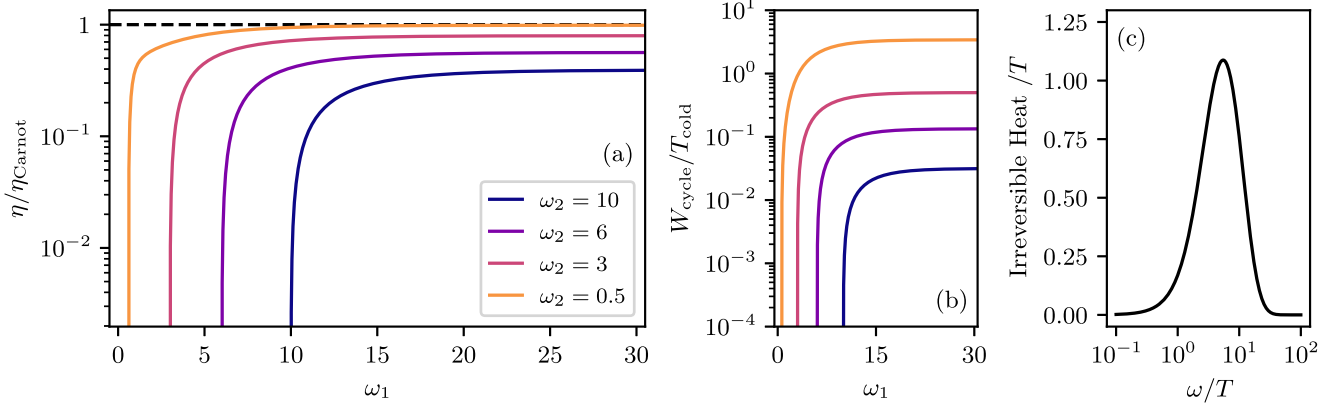


FIG. 2. Efficiency, work, and irreversible heat for a single qubit heat engine of the first type. ω_1 and ω_2 are the gaps of the initial and final Hamiltonians, respectively, $\hbar = 1$, $k_B = 1$, and $T_{\text{cold}} = 1$ in arbitrary units so that all energy quantities are expressed in units of T_{cold} . (a) The efficiency of the cycle: as $\hbar\omega_2 \ll k_B T_{\text{cold}}$ and $\hbar\omega_1 \gg k_B T_{\text{hot}}$ Carnot's efficiency is approached. (b) Deterministic work drawn from the cycle. (c) Irreversible heat dissipated during the thermalization steps (either $B \rightarrow C$ or $D \rightarrow A$) as a function of the corresponding gap ω (ω_1 or ω_2).

Thus, in this case, heat and work are related by $Q = \Delta E - \langle W \rangle$ and the efficiency can be generically written as

$$\eta = 1 - \frac{T_{\text{cold}}[S_B - S_D] + |\delta Q_{BC}|}{T_{\text{hot}}[S_B - S_D] - |\delta Q_{DA}|}, \quad (8)$$

where we define $|\delta Q_{DA}| \equiv T_{\text{hot}}(S_A - S_D) - |Q_{DA}|$ and $|\delta Q_{BC}| \equiv |Q_{BC}| - T_{\text{cold}}(S_B - S_C)$. Then, $|\delta Q|$ is the difference between the heat exchange of the stroke (with bounded fluctuations) and the heat exchange of an ideal stroke when arbitrary large fluctuations are allowed (see Appendix A). Thus Carnot's efficiency is attained as both heat differences tend to zero, $|\delta Q| \rightarrow 0$.

For instance, using the analytical formula for the average work $\langle W \rangle$ with bounded fluctuations in the case of two-level systems [39], we can study the efficiency for a specific cycle. In Fig. 3 we show the efficiency as a function of the size of the fluctuations, ΔW , for the single qubit heat engine. There we can see that the efficiency is increased as we allow fluctu-

ations, and for large fluctuations Carnot efficiency is attained. Furthermore, even when a small amount of fluctuations is allowed the efficiency is drastically improved.

IV. CYCLES IN TERMS OF NONEQUILIBRIUM STATES

We will now show a cycle that generalizes the previous one and can be defined in terms of nonequilibrium states with a fixed Hamiltonian. As we mention before, deterministic work extraction in a process that occurs at a fixed Hamiltonian requires an initial non-full-rank state for \mathcal{S} . In addition, in order to close the cycle, the creation of this nonequilibrium state is also required. Thus, due to the intrinsic irreversibility of the single-shot transformations, this poses a problem to our task. However, there is a way to circumvent this issue; to this end we will first introduce a set of states that we call reversible.

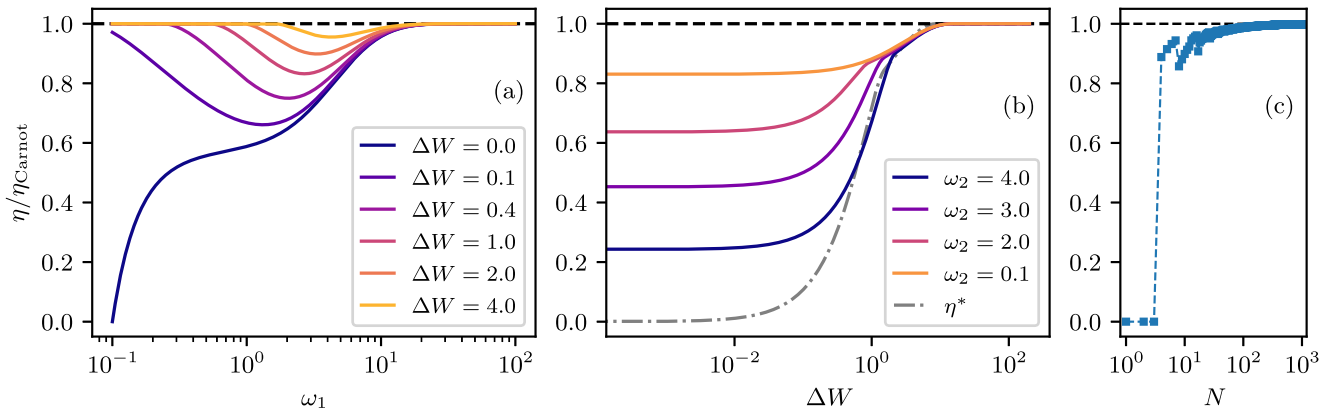


FIG. 3. Efficiency for single qubit heat engines of the first type when fluctuations are allowed [(a) and (b)] and the efficiency for the many qubits engine (c). We use the same convention of Fig. 2 for numerics and we fix $\omega_2 = 5$. (a) Efficiency in terms of the initial gap ω_1 for different fluctuation sizes ΔW (by this we mean that the extracted work must lay within $\langle W_{\text{cycle}} \rangle \pm \Delta W$). By allowing fluctuations the efficiency is increased, and for large values of ΔW we eventually recover Carnot efficiency. (b) Efficiency in terms of ΔW ; η^* is the efficiency of the single qubit heat engine proposed in [39] that works with a fixed Hamiltonian. For small ΔW , the efficiency of our cycle has a nonzero value, while η^* vanishes since the cycle is unable to extract deterministic work. (c) Efficiency for the correlated N -qubit engine; as N increases Carnot's efficiency is rapidly approached.

We will say that a state σ is *reversible* if its work of formation equals its extractable work,

$$W_{\text{form}}(\sigma) = W_{\text{ext}}(\sigma). \quad (9)$$

The following results provide a complete characterization of this set of states.

Proposition. Consider a block-diagonal state σ with support

$$\text{supp}(\sigma) = \bigoplus_E \mathcal{U}_E, \quad (10)$$

where \mathcal{U}_E is a subspace of the energy shell E . Then, σ is a reversible at a background inverse temperature β if and only if it has a thermal-like distribution over $\text{supp}(\sigma)$, i.e.,

$$\sigma = \frac{1}{Z} \sum_E e^{-\beta E} \Pi_{\mathcal{U}_E}, \quad (11)$$

where $\Pi_{\mathcal{U}_E}$ is the projector over \mathcal{U}_E and Z is a normalization constant given by $Z = \sum_E \dim(\mathcal{U}_E) e^{-\beta E}$.

Notice that these states have a uniform distribution over each \mathcal{U}_E . Some key properties of reversible states (which are shown in Appendix B along with the proof of the proposition) are listed below.

(1) The work of formation and the extractable work of the reversible states are equal to the standard free energy difference

$$W_{\text{form}}(\sigma) = W_{\text{ext}}(\sigma) = F(\sigma) - F(\tau(\beta)), \quad (12)$$

where $\tau(\beta)$ is the thermal state at inverse temperature of the bath β .

(2) Any state with the same support of σ can be transformed into σ via a single-shot thermal operation at no work cost.

(3) For any state ρ which has the same support of σ and $\rho \neq \sigma$: $W_{\text{ext}}(\rho) = W_{\text{ext}}(\sigma)$ and $W_{\text{form}}(\rho) > W_{\text{form}}(\sigma)$.

Notably, there is a subset of the reversible states that has an interesting physical interpretation [55] and will be important in what follows. This subset is composed by the states whose energy levels are uniformly populated or not populated at all; that is, $\dim(\mathcal{U}_E) = 0$ or $\dim(\mathcal{U}_E) = g(E)$, where $g(\cdot)$ is the degeneracy of the energy shell E . Thus the states of this subset are fully characterized by the set of energies \mathcal{U} that define their support and they can be written as

$$\tau|_{\mathcal{U}}(\beta) = \frac{1}{Z_{\mathcal{U}}} \sum_{E \in \mathcal{U}} e^{-\beta E} \Pi_E. \quad (13)$$

Now we are ready to introduce the second set of heat engines, also illustrated in Fig. 1. We will consider the system \mathcal{S} as an arbitrary finite dimensional system (of dimension greater than 2) with a given Hamiltonian. Without loss of generality (see Appendix B) we will assume that initially \mathcal{S} is in a nonequilibrium reversible state (i.e., not a thermal state) at inverse temperature β_{hot} . During the first stroke, \mathcal{S} goes from $\tau|_{\mathcal{U}}(\beta_{\text{hot}})$ to $\tau|_{\mathcal{V}}(\beta_{\text{hot}})$ in contact with the hot bath. As we mentioned, these two states are completely determined by their respective supports (\mathcal{U} and \mathcal{V}) and temperature. Since the initial and final states are reversible, the total amount of deterministic work that is drawn in this step equals the standard free energy difference: $W_{AB} = F_A - F_B =$

$F(\tau|_{\mathcal{U}}(\beta_{\text{hot}})) - F(\tau|_{\mathcal{V}}(\beta_{\text{hot}}))$. The second stroke, $B \rightarrow C$, is such that the system goes from $\tau|_{\mathcal{V}}(\beta_{\text{hot}}) \rightarrow \tau|_{\mathcal{V}}(\beta_{\text{cold}})$ in contact with the cold bath. This step generalizes the thermalization stroke of the previous cycle and, like in that case, it can be achieved at no work cost (see Property 2). The remaining strokes are defined in a similar way. During $C \rightarrow D$, the system is in contact with the cold bath and the transformation $\tau|_{\mathcal{V}}(\beta_{\text{cold}}) \rightarrow \tau|_{\mathcal{U}}(\beta_{\text{cold}})$ is done at a deterministic work cost equal to the free energy difference $W_{DC} = F_D - F_C$. Finally, the transformation $D \rightarrow A$, where the system returns to its initial state $\tau|_{\mathcal{U}}(\beta_{\text{cold}}) \rightarrow \tau|_{\mathcal{U}}(\beta_{\text{hot}})$, is done in contact with the hot bath at no work cost. Therefore, the expressions for the net extracted work and the efficiency have the same form as before [Eqs. (4) and (6)] except that in this case the labels A, B, C, D refers to the nonequilibrium states we define above. Notice that the previous cycle can also be considered a particular realization of this more general cycle. Indeed, when one adds the clock degree of freedom, the complete state of system plus clock can be considered as particular instances of the reversible states we defined before.

This more general cycle is particularly useful to analyze the behavior of the heat engine when the working medium \mathcal{S} is composed by N identical subsystems. In [55], the presence of correlations in single-shot transformations was studied. In particular, it was shown that for every single particle state ρ there exists a correlated N -partite state $\rho^{(N)}$, such that the reduced state of each subsystem is ρ and $W_{\text{form}}(\rho^{(N)}) \leq N W_{\text{form}}(\rho)$. Notably, the set of reversible states of Eq. (13) appears naturally in this context as the set of states that minimizes the corresponding work of formation. Interestingly, if we consider heat engines working between these reversible states, it is possible to demonstrate that for large N the efficiency converges to Carnot. Furthermore, these states hold an amount of correlations that scales as $O(\ln N)$. Therefore, if we consider a working medium composed of N particles, we recover Carnot efficiency allowing an amount correlations per particle that it is vanishing small in the large N limit, as can be observed, for example, in panel (c) of Fig. 3 (see Appendix C for details). Moreover, one can show that, in the limit $N \rightarrow \infty$, $W(\rho^{(N)})/N \rightarrow \Delta F = F(\rho) - F(\tau)$, so that the extracted work per particle in this cycle is simply given by the standard free energy of the reduced state.

V. DISCUSSION

It is worth comparing our results with previous single-shot proposals that were unable to extract deterministic work. In [33] a single-shot engine that mimics the Carnot cycle was introduced; it consisted of two strokes in contact with heat baths plus two adiabatic transformations. Our results indicate that, if one replaces the adiabatic strokes with thermalizations (at no work cost), single-shot deterministic work extraction can be achieved. Another qubit heat engine with two strokes was introduced in [39]. There the transformations in contact with the heat baths were done at fixed Hamiltonian and it was shown that no deterministic work can be extracted. However, when fluctuations in work were allowed a nonzero average work can be extracted at finite efficiency. Here we showed that deterministic work extraction with fixed Hamiltonian requires strokes with nonequilibrium states. In Fig. 3(b) we plot the

efficiency η^* of the heat engine introduced in [39] along with the efficiency of our first cycle for a two-level system. Besides the difference in efficiency, we should also stress that in our cycle the amount of deterministic work does not change when fluctuations are allowed; in fact the efficiency is improved because an additional fluctuating work is extracted during the thermalization stroke. Finally, in [52,53] it was shown that no deterministic heat engine exists if the cold bath has finite size. This is an interesting approach which is different from the one considered here and in the other proposals. Our scheme requires infinite hot and cold baths, which is very much in line with traditional formulations of heat engines.

Here we have introduced thermodynamic cycles that allow deterministic work extraction in the single-shot regime. It is worth noting that, while we have focused on an engine that extracts work, the same idea can be used to design a single-shot refrigerator that has a deterministic work cost of operation (although the heat removed from the cold bath will still have fluctuations). Indeed both strokes, $A \rightarrow B$ and $C \rightarrow D$, are reversible and therefore can be inverted, while the thermalization steps $B \rightarrow C$ and $D \rightarrow A$ are irreversible. Therefore, to operate as a refrigerator these transformations have to be changed. However, it is easy to check that swapping the baths at those steps (so that $C \rightarrow B$ is done at T_{hot} and $A \rightarrow D$ at T_{cold}) is enough. We have also shown that optimal efficiency can be approached by allowing fluctuations in the extracted work or in the limit $N \rightarrow \infty$ when the working medium is composed of many particles. In this last example, the cycle is such that the work extracted per particle depends only on the standard nonequilibrium free energy of the reduced system (which can be chosen arbitrarily), recovering standard results of heat engines in the macroscopic limit.

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APPENDIX A: BOUND ON THE EFFICIENCY

Here we show a simple lower bound on the difference between the efficiency of our first cycle Eq. (6) and Carnot's efficiency. We showed that

$$\eta = 1 - \frac{T_{\text{cold}}[S_C - S_D] + E_B - E_C}{T_{\text{hot}}[S_B - S_A] + E_A - E_D}, \quad (\text{A1})$$

$$= 1 - \frac{T_{\text{cold}}[S_C - S_D] + |Q_{BC}|}{T_{\text{hot}}[S_B - S_A] + |Q_{DA}|}, \quad (\text{A2})$$

where the last equation is written in terms of the heat exchange over the strokes BC and DA . Notice also that this last expression is valid even when one allows fluctuations in work. Thus the efficiency when we allow fluctuations in the work depends on the value of the heat exchanged over those strokes.

According to the first law $Q = \Delta E - \langle W \rangle$. Then, if we do not allow fluctuations, the amount of dissipated heat in the BC stroke ($E_C < E_B$) equals $|Q_{BC}| = E_B - E_C$, since one cannot extract any deterministic work. On the other hand, we showed that if one allows arbitrary large fluctuations

in the value of work, the optimal transformation allows one to extract an amount of work equal to the free energy difference $|W| = (E_B - E_C) - T_{\text{cold}}(S_B - S_C)$ and therefore the heat exchange in this case would be $|Q_{BC}^{\text{opt}}| = T_{\text{cold}}(S_B - S_C)$. In general, $|Q_{BC}| = |\Delta E_{BC}| - |W_{BC}|$; therefore, $T_{\text{cold}}(S_B - S_C) \leq |Q_{BC}| \leq E_B - E_C$. Now, we can define

$$|\delta Q_{BC}| \equiv |Q_{BC}| - T_{\text{cold}}(S_B - S_C) \quad (\text{A3})$$

as the difference between the heat exchange in BC and the heat exchange in the optimal stroke. Therefore, $0 \leq |\delta Q_{BC}| \leq (E_B - E_C) - T_{\text{cold}}(S_B - S_C) \equiv \Delta F_{BC}$. Analogously we can define

$$|\delta Q_{DA}| \equiv T_{\text{hot}}(S_A - S_D) - |Q_{DA}| \quad (\text{A4})$$

for the stroke AB . Notice that in this case $|Q_{DA}| = |\Delta E_{DA}| + |W_{DA}|$ and $(E_A - E_D) \leq |Q_{DA}| \leq T_{\text{hot}}(S_A - S_D)$, which is the reason why we define the difference in heat with the minus sign. In this case $0 \leq |\delta Q_{DA}| \leq (E_D - E_A) - T_{\text{hot}}(S_D - S_A) \equiv \Delta F_{DA}$. Therefore, in general, we can rewrite the efficiency as

$$\eta = 1 - \frac{T_{\text{cold}}[S_B - S_D] + |\delta Q_{BC}|}{T_{\text{hot}}[S_B - S_D] - |\delta Q_{DA}|}. \quad (\text{A5})$$

The difference with Carnot's efficiency can be written as

$$\Delta \eta \equiv \eta_C - \eta = \frac{|\delta Q_{BC}| + \frac{T_{\text{cold}}}{T_{\text{hot}}} |\delta Q_{DA}|}{T_{\text{hot}}[S_B - S_D] - |\delta Q_{DA}|}. \quad (\text{A6})$$

Thus the efficiency approaches Carnot's as both δQ tend to zero. A simple lower bound to this difference can be easily obtained:

$$\Delta \eta \geq \frac{|\delta Q_{BC}|}{T_{\text{hot}}[S_B - S_D]}. \quad (\text{A7})$$

APPENDIX B: PROPERTIES OF REVERSIBLE STATES

Proof. (Proposition in the main text). We will start by showing that any state having a thermal-like distribution over a reduced support is reversible. First, notice that all nonzero eigenvalues $\lambda_{E,g}$ of the states σ in Eq. (11) satisfy $\lambda_{E,g} e^{\beta E} = 1/Z$. Then,

$$\begin{aligned} W_{\text{form}}(\sigma) &= \beta^{-1} \ln \max_{E,g} \lambda_{E,g} e^{\beta E} - F(\tau(\beta)) \\ &= -\beta^{-1} \ln Z - F(\tau(\beta)) \\ &= -\beta^{-1} \ln \sum_E \dim(\mathcal{U}_E) e^{-\beta E} - F(\tau(\beta)) \\ &= W_{\text{ext}}(\sigma), \end{aligned} \quad (\text{B1})$$

which shows that σ is a reversible state.

Let us prove now that *all* reversible states have the form of Eq. (11). Consider ρ a reversible state with

$$\text{supp}(\rho) = \bigoplus_E \mathcal{U}_E^\rho, \quad (\text{B2})$$

where $\mathcal{U}_E^\rho = \text{supp}(\rho) \cap \{|\psi\rangle : H|\psi\rangle = E|\psi\rangle\}$. Now let us define the thermal-like state σ on the support of ρ , that is,

$$\sigma = \frac{1}{Z_\sigma} \sum_E e^{-\beta E} \Pi_{\mathcal{U}_E^\rho}. \quad (\text{B3})$$

Since ρ and σ have the same support, they have also the same extractable work, $W_{\text{ext}}(\sigma) = W_{\text{ext}}(\rho)$. As both states are reversible (ρ by hypothesis),

$$W_{\text{form}}(\rho) = W_{\text{ext}}(\rho) = W_{\text{ext}}(\sigma) = W_{\text{form}}(\sigma). \quad (\text{B4})$$

This proves that both states also have the same work of formation. Based on the definition of work of formation, this implies

$$\max_{E,g} \lambda_{E,g}^\rho e^{\beta E} = \max_{E,g} \lambda_{E,g}^\sigma e^{\beta E} = \frac{1}{Z_\sigma}, \quad (\text{B5})$$

where $\lambda_{E,g}^\rho, \lambda_{E,g}^\sigma$ are the eigenvalues of ρ and σ with associated energy E , respectively. This last expression implies that $\lambda_{E,g}^\rho \leq e^{-\beta E}/Z_\sigma = \lambda_{E,g}^\sigma$. If the last inequality is strict for at least one value of (E, g) , then we will have

$$1 = \text{tr}(\rho) = \sum_{E,g} \lambda_{E,g}^\rho < \sum_{E,g} \lambda_{E,g}^\sigma = 1, \quad (\text{B6})$$

which is a contradiction. We conclude $\lambda_{E,g}^\rho = \lambda_{E,g}^\sigma$ and therefore $\rho = \sigma$.

Now we prove properties (1)–(3) of reversible states. Notice that, since σ has a Gibbs distribution over the subspace \mathcal{U} , then clearly the free energy is

$$F(\sigma) = -k_B T \ln \sum_E \dim(\mathcal{U}_E) e^{-\beta E_n}. \quad (\text{B7})$$

Putting all this together means that $W_{\text{form}}(\sigma) = W_{\text{ext}}(\sigma) = F(\sigma) - F(\tau)$. This proves property (1) for this class of reversible states.

For property (2), given any state ρ with support $\text{supp}(\rho)$ and such that $[\rho, H] = 0$, we want to show that the transformation $\rho \rightarrow \sigma$ is allowed by thermal operations. Showing this is equivalent to showing that ρ thermomajorizes σ [33]. Now, given that both states have the same support, the thermomajorization condition is the same as the one that is obtained for two full-rank probability vectors with the same distribution that ρ and σ have over $\text{supp}(\rho)$. Within this subspace, σ has a thermal distribution and therefore it is majorized by *any* vector with the same support, in particular ρ .

For property (3), since ρ and σ have the same support, they have the same extractable work $W_{\text{ext}}(\rho) = W_{\text{ext}}(\sigma)$. Furthermore, we have shown in property (2) that any state ρ with the same support as σ can be converted into the latter at no cost. Therefore, the cost of formation of any state ρ must be at least that of σ , $W_{\text{form}}(\rho) \geq W_{\text{form}}(\sigma)$. Since the only reversible state with the same support of σ is σ , we have that the last inequality is strict.

In light of these properties, if we have the system initially in an arbitrary nonequilibrium state ρ with nonfull support, we can always transform it to the reversible state, $\tau|_{\mathcal{U}_\rho}$, with same support \mathcal{U}_ρ . In this way, one can extract the same amount of work from both states, although the reversible one has a smaller work of formation. Analogously, we can easily see that, if the system is initially in a thermal state, we can transform it to an arbitrary reversible state using an amount of energy equal to its work of formation (this energy can be recovered after some finite number of cycles). Thus, without loss of generality, we will consider that the system is initially in a nonequilibrium reversible state (i.e., not a thermal state).

APPENDIX C: CORRELATED SUBSYSTEMS

Consider a working medium of N noninteracting identical qubits. If the Hamiltonian of the qubits has a gap $\hbar\omega$, then the N qubit system will have an energy spectrum $\{E_m = m\hbar\omega, m = 0, \dots, N\}$, each with degeneracy $g(m) = \binom{N}{m}$. We will focus on states $\rho^{(N)}$ of the N qubits such that the local density matrix of all qubits is the same. Given that we will restrict ourselves to states diagonal in the energy eigenbasis, these local states can be parametrized by the excited state probability p as $\rho = p|1\rangle\langle 1| + (1-p)|0\rangle\langle 0|$, where $\{|0\rangle, |1\rangle\}$ is an orthonormal basis such that $H = \hbar\omega|1\rangle\langle 1|$.

In [55] it was shown that one can reduce the work of formation of such states if correlations between subsystems are allowed. That is,

$$W_{\text{form}}(\rho^{(N)}) < W_{\text{form}}(\rho^{\otimes N}) = N W_{\text{form}}(\rho), \quad (\text{C1})$$

where $\rho^{(N)}$ is a state where each qubit has a local density matrix equal to ρ . In particular, for certain single qubit states ρ , the correlated state $\rho^{(N)}$ that minimizes $W_{\text{form}}(\rho^{(N)})$ is a reversible state. This happens, for example, for local density matrices $\rho_k = p_k|1\rangle\langle 1| + (1-p_k)|0\rangle\langle 0|$, $k = 1, \dots, N-1$, with

$$p_k = \frac{\sum_{m=0}^k m \binom{N}{m} e^{-m\beta\hbar\omega}}{N \sum_{m=0}^k \binom{N}{m} e^{-m\beta\hbar\omega}}. \quad (\text{C2})$$

In this case corresponding reversible correlated state $\rho^{(N)}$ has a Gibbs-like thermal distribution over the support $\mathcal{U}_k = \{|E = m\hbar\omega, g\rangle, g = 1, \dots, g(m); m = 0, \dots, k\}$. All relevant thermodynamic quantities of these states are determined by their effective partition function $Z_k(\beta)$ given by

$$Z_k(\beta) = \sum_{m=0}^k \binom{N}{m} e^{-m\beta\hbar\omega}. \quad (\text{C3})$$

In the following, we will show results for the large N limit, so it is useful to rewrite this partition function as

$$Z_k(\beta) = [Z(\beta)]^N \sum_{m=0}^k \binom{N}{m} p_\beta^m (1-p_\beta)^{N-m}, \quad (\text{C4})$$

where $p_\beta = e^{-\beta\hbar\omega}/(1 + e^{-\beta\hbar\omega})$ is the excited state probability for a single qubit in thermal equilibrium and $Z(\beta) = 1 + e^{-\beta\hbar\omega}$ its respective partition function. Notice that the second factor in (C4) is a tail sum of a binomial distribution characterized by N trials with success probability p_β . We will base our large N approximation on well known approximations for binomial tails.

Let $\{k_N \in \mathbb{N}, N \in \mathbb{N}_0\}$ be a sequence such that $k_N/N \rightarrow q$, when $N \rightarrow \infty$, for some $0 < q < p_\beta$. We then have the following bounds on the binomial tail: $B(p_\beta, k_N, N) = \sum_{m=0}^{k_N} \binom{N}{m} p_\beta^m (1-p_\beta)^{N-m}$ [56], Lemma 4.7.2; there the bounds are derived for the upper tail of the distribution; that is, for $B(1-p_\beta, N-k_N, N)$, it is easy to check that they also hold for the lower tail of the distribution $B(p_\beta, k_N, N)$. Thus

$$\frac{1}{\sqrt{8Nq(1-q)}} e^{-ND(q\|p_\beta)} \leq B(p_\beta, k_N, N) \leq e^{-ND(q\|p_\beta)}, \quad (\text{C5})$$

where $D(q\|p) = q \ln(q/p) + (1-q)\ln[(1-q)/(1-p)]$ is the binary relative entropy. Therefore, asymptotically we have that [56]

$$\lim_{N \rightarrow \infty} -\frac{1}{N} \ln B(p_\beta, k_N, N) = D(q\|p_\beta) \quad (\text{C6})$$

and the convergence rate is $O(\log N/N)$. Applying these results to the logarithm of the partition function (C4) of the reversible state we have the asymptotic behavior

$$-\frac{1}{N} \ln Z_k(\beta) \approx -\ln Z(\beta) + D(q\|p_\beta). \quad (\text{C7})$$

Therefore, the average energy per qubit is

$$\begin{aligned} \frac{1}{N} \langle E \rangle_k &= -\frac{1}{N} \frac{\partial}{\partial \beta} \ln Z_k(\beta) \\ &\approx p_\beta \hbar \omega + \frac{\partial}{\partial \beta} D(q\|p_\beta) \end{aligned} \quad (\text{C8})$$

$$= p_\beta \hbar \omega + q \hbar \omega - p_\beta \hbar \omega = q \hbar \omega. \quad (\text{C9})$$

Notice that the average energy of the system can also be written in terms of the local state probability p_k as $\langle E \rangle_k = N p_k \hbar \omega$. Therefore, this implies that in the large N limit $p_k \rightarrow q$, so that the parameter q determines the asymptotic local state of the qubits. Here all convergence rates are of order $O(\log N/N)$. Similarly, for the free energy of the reversible state we have that

$$F_k(\beta) = NF(q, \beta) + O(\log N), \quad (\text{C10})$$

where $F(q, \beta)$ is the standard free energy of the asymptotic single qubit state $\rho(q) = q|1\rangle\langle 1| + (1-q)|0\rangle\langle 0|$. In [55] it is

further shown that the total correlations per particle in these reversible states vanish in the large N limit as $O(\log N/N)$.

In our heat engine cycle we need to have reversible states at two different temperatures, β_{hot} and β_{cold} , and different supports \mathcal{U} and \mathcal{V} for each number of subsystems N . If we choose our sequence of supports \mathcal{U}_{k_N} and \mathcal{V}_{l_N} such that $k_N/N \rightarrow q$ and $l_N/N \rightarrow r$ with $0 < q < r < \min(p_{\beta_{\text{hot}}}, p_{\beta_{\text{cold}}})$, we can then apply the above asymptotic expressions for all four reversible states. In particular, this means that the work extracted in each cycle per particle is

$$\frac{W_{\text{cycle}}}{N} \approx F(q, \beta_{\text{hot}}) - F(r, \beta_{\text{hot}}) - F(q, \beta_{\text{cold}}) + F(r, \beta_{\text{cold}}), \quad (\text{C11})$$

so that we simply extract the free energy difference of the local states. Notice that these local states have full support and therefore it would be impossible to deterministically extract any energy from them without allowing correlations. Furthermore, notice that in the large N limit we have that the average energy per particle (C8) does not depend on temperature. This means that the reversible states at points B and C of the cycle (or A and D) have, up to $O(\log N/N)$ corrections, the same energy. This implies that the irreversible heat per particle vanishes in the large N limit, $Q_{BC} \approx 0$, $Q_{DA} \approx 0$. As discussed in the main text, this implies that we have Carnot efficiency. Indeed it is simple to check via direct substitution of the above asymptotic expressions that

$$\lim_{N \rightarrow \infty} \eta = \eta_{\text{Carnot}}. \quad (\text{C12})$$

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