Heat engines with single-shot deterministic work extraction

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We introduce heat engines working in the nano-regime that allow to extract a finite amount of deterministic work. 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 recovered for unbounded fluctuations, while certain amount of deterministic work is drawn from the cycle. Finally, we show that if the working medium is composed by many particles, by creating an amount of correlations between the subsystems that scales logarithmically with their number, Carnot’s efficiency can also be approached in the asymptotic limit along with deterministic work extraction.

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 small number of systems in the quantum realm [13]. Pursuing the identification of the limitations and advantages of these devices that operates in the nano-regime, 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 realisations 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 either the work that can be extracted from a given transformation, or the work that needs to be invested to generate it. Thus, naturally, one expects a poorer performance for heat engines working in such regime. However, the existing results seems suggest that it is not even possible to design a cycle able extract a finite amount of deterministic work in the single-shot regime [31, 39, 50, 53].

Here we show that in fact one can define such heat engines in the single-shot regime. Specifically, we introduce thermodynamic cycles that allow to extract a deterministic amount of work from a nanoscale system (working medium) that is 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 is subjected to a driving, or in terms of a set of non-equilibrium 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.

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 $T_{\text{hot}}$ and $T_{\text{cold}}$ (with $T_{\text{cold}} < T_{\text{hot}}$) 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 $\tau_{B}$. Work will be quantified by considering an additional degree of freedom, that acts as a battery [32, 33]. The battery is modelled as quantum system $W$ with its own Hamiltonian $H_W$ that, in a deterministic (fluctuation
free) transformation, starts and ends up in a pure energy eigenstate of \( H_W \). 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. Thus, for deterministic work extraction, a two-level system will be enough.

The cycles we will introduce can be generically described by a four stroke process as it is 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 \([U, H_S + H_W + H_B] = 0\), where \( H_S \) is the Hamiltonian of the systems \( S \) and \( H_B \) is the Hamiltonian of the corresponding bath \( B \). 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 working medium. In this way, an initial state \( \eta \) (system + battery) can be transformed into a final one \( \sigma \) after tracing over the degrees of freedom of the bath: \( \sigma = \tau_B[U(\eta \otimes \tau_B)U^\dagger] \), this is called a thermal transformation and will be denoted by \( \eta \rightarrow \sigma \) \(^33,^34\).

In this way, each stroke can be generically described by a thermal transformation. For a finite dimensional system with Hamiltonian \( H_S = \sum_E E \Pi_E \), where \( \Pi_E \) 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) the maximum amount of deterministic work \( W_{\text{ext}} \) that can be extracted in contact with a reservoir at temperature \( T \) is given by

\[
W_{\text{ext}}(\rho) = F_0(\rho) - F(\tau_S),
\]

where \( F_0(\rho) = -\beta^{-1} \log \sum_{E \in \text{supp}(\rho)} e^{-\beta E}, \beta = (k_BT)^{-1} \) with \( k_B \) the Boltzmann constant, \( \text{supp}(\rho) \) is the support of the state \( \rho \), and \( F(\tau_S) \) is the standard free energy of the thermal state \( \tau_S = e^{-\beta H_S}/Z_S \) given by \( F(\tau_S) = -\log Z_S \). This is called the extractable work, and is obtained by maximizing \( W \) over the thermal transformation \( \rho \otimes |0\rangle\langle 0| \rightarrow \tau_S \otimes |W\rangle \langle W| \), with \( H_W = W |W\rangle \langle W| \). 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 an non-eigenstate of \( \rho \) is created out of an initial thermal state, requires a minimum amount of deterministic work

\[
W_{\text{form}}(\rho) = F_\infty(\rho) - F(\tau_S),
\]

where \( F_\infty = \beta^{-1} \log \max_{E,g} \lambda_{E,g} e^{\beta E} \) which is the so-called work of formation. Remarkably, \( W_{\text{form}}(\rho) \geq W_{\text{ext}}(\rho) \) (the inequality is strict except for very specific cases that we will discuss later) which means there is a fundamental irreversibility in the single-shot regime \(^33,^34\). Under all these assumptions, we will consider limits for microscopic heat engines.

**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 with a fixed Hamiltonian starting from an initial thermal state is useless for deterministic work extraction, since no work can be extracted from full rank states. However, we can overcome this issue by introducing a driving, meaning that during the transformation the Hamiltonian of the system changes from \( H_1 \) to \( H_2 \). This thermal transformation can be modelled by introducing an auxiliary two-level system \( C \) with trivial Hamiltonian that acts as a clock \(^33,^34\). Then, by defining the Hamiltonian of the working medium as \( H_{SC} = H_1 \otimes |0\rangle\langle 0| + H_2 \otimes |1\rangle\langle 1| \), with \(|0\rangle, |1\rangle \) an orthonormal basis of \( C \), the above work extraction process can be formally expressed as

\[
\tau_{S,1} \otimes |0\rangle\langle 0| \rightarrow \tau_{S,2} \otimes |1\rangle\langle 1| \rightarrow W \rightarrow \tau_{S,1} \otimes |0\rangle\langle 0|, \tag{3}
\]

where \( \tau_{S,1} \) is the thermal equilibrium state of \( S \) with Hamiltonian \( H_1 \). This type of transformation resembles the classical isothermal expansion of a gas. 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 \( \Delta W = \Delta F = F(\tau_{S,2}) - F(\tau_{S,1}) \). 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 analyse the cycle in detail, as we said before. During the first stroke the system is driven from \( H \rightarrow H_2 \) in contact with the hot bath and ends up at \( B \) in equilibrium with \((H_2, T_{\text{hot}})\). The extracted work after this step is equal to \( \Delta F_{AB} = F_A - F_B \) (where \( F(I) \) 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 thermalises, thus the state of the system at \( C \) is \((H_2, T_{\text{cold}})\). 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 consequence of the fact that the thermal state is \textit{thermo-majorized} 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 \((H_1, T_{\text{cold}})\). Finally, the system is brought again in contact with the hot bath and thermalises 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:

\[
W_{\text{cycle}} = F_A - F_B - F_D + F_C. \tag{4}
\]

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

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 \( \Delta E \), then the heat \( Q \) exchanged with the reservoir during the transformation is

\[
Q = \Delta E - W. \tag{5}
\]

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

\[
\eta = \frac{W_{\text{cycle}}}{Q_{\text{hot}}} = 1 - \frac{Q_{\text{cold}}}{Q_{\text{hot}}}
= 1 - \frac{T_{\text{cold}} [S_D - S_C] + E_C - E_B}{T_{\text{hot}} [S_A - S_B] + E_D - E_A}, \tag{6}
\]

where \( S(I) \) and \( E(I) \) 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, \( \eta < \eta_{\text{Carnot}} = 1 - T_{\text{cold}}/T_{\text{hot}} \). 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 \( B \), \((H_2, T_{\text{hot}})\) is a non-equilibrium 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 \( S \). 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. It is also worth noting that this cycle is very reminiscent of the Stirling engine [32]. This classical cycle also contains irreversible thermalization steps that reduce the efficiency. However, by adding an auxiliary system, typically called regenerator, reversibility and Carnot’s efficiency could in principle be recovered [34].

Interestingly, there is another way to approach Carnot’s efficiency in this cycle. This is at the expense of allowing some fluctuations in the work extraction. Extensions of single-shot thermodynamics with bounded fluctuations in work has been thoroughly studied in [39], and 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, and if we allow arbitrary large fluctuations the mean value of this work equals the free energy difference: $(W_{BC}) = F_B - F_C$ and $(W_{DA}) = F_D - F_A$. It is then straightforward to see that in this limit the efficiency 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. Thus, if the size of fluctuations is bounded, the average work that can be extracted during the thermalization step is $(W) < \Delta F$, and there is an improvement in the efficiency. For a detailed analysis, a closed form of the average work with bounded fluctuations can be obtained for two-level systems [39]. In Fig. 3 we show the efficiency as a function of the size of the fluctuations, $\Delta W$, for the single qubit heat engine. There we can see the efficiency increases as we allow fluctuations, and for large fluctuations Carnot efficiency is approached. Furthermore, even for a small amount of fluctuations the efficiency is drastically improved.

Cycles in terms of non-equilibrium states. – We will now show a cycle that generalizes the previous one, and can be defined in terms non-equilibrium states with a fixed Hamiltonian. Deterministic work extraction with a fixed Hamiltonian requires an initial non-full rank state for $S$, and at the end of the cycle it is required the creation of this non-equilibrium state. However, since in general the work of formation is larger than the extractable work, this poses an obstacle. To see how we can circumvent this issue we will introduce the family of reversible states [55]. We will say that a state $\sigma$ is reversible if its work of formation equals its extractable work:

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

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

Proposition. Consider a block-diagonal state $\sigma$ with support

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

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

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

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

FIG. 3. Efficiency of a single qubit heat engine of the first type when fluctuations are allowed. We use the same convention of Fig. 2 for numerics and we fix $\omega_2 = 5$. (a) shows the efficiency as a function of the initial gap $\omega_1$ for different fluctuation sizes $\Delta W$ (by this we mean that the extracted work must lay within $(W_{\text{cycle}}) \pm \Delta W$). Allowing fluctuations enhance the efficiency not only for large values of $\omega_1$ (as expected from Fig. 2), but also for small ones, and as $\Delta W$ increases we eventually recover Carnot efficiency for all $\omega_1$. This can also be seen in panel (b) where it is shown the efficiency as a function of $\Delta W$ for different values of $\omega_1$. $\eta^*$ is the efficiency of the single qubit heat engine proposed in [39] working with a fixed Hamiltonian. For small values of $\Delta W$, the efficiency our cycle has a finite value while $\eta^*$ vanishes since it is not the cycle is unable to extract deterministic work.
Notice that these states have a uniform distribution over each $\mathcal{U}_E$. Some key properties of reversible states (which we prove in the Supplementary Material) are listed below:

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

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

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

2. Any state with the same support of $\sigma$ can be transformed into $\sigma$ via a single-shot thermal operations at no work cost.

3. Any state $\rho$ with the same support of $\sigma$ and $\rho \neq \sigma$, has $W_{\text{ext}}(\rho) = W_{\text{ext}}(\sigma)$ and $W_{\text{form}}(\rho) > W_{\text{form}}(\sigma)$.

A certain family of the reversible states that has an interesting physical interpretation [55], and we will use bellow, corresponds to the case where energy level is uniformly populated or not populated at all, that is, $\dim(\mathcal{U}_E) = 0$ or $\dim(\mathcal{U}_E) = g(E)$, with $g(\cdot)$ the degeneracy. Each state of this set is fully characterized by the set of energies $\mathcal{U}$ that define their support, and can be written as:

$$\tau|_{\mathcal{U}}(\beta) = \frac{1}{Z_{\mathcal{U}}} \sum_{E \in \mathcal{U}} e^{-\beta E} \Pi_E.$$  \hspace{1cm} (10)

Now we are ready to introduce the second set of heat engines, illustrated in Fig. [3]. We will consider the system $S$ as an arbitrary finite dimensional system (as it will become clear later we cannot define a non-trivial single qubit heat engine for this cycle) with a given Hamiltonian. Without loss of generality (see the SM) we will assume that initially is in an non-equilibrium reversible state (i.e. not a thermal state) at inverse temperature $\beta_{\text{hot}}$. During the first stroke, $S$ 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 non-equilibrium 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 analyse the behaviour of these heat engines when the working medium $S$ 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 $\rho$ there exists a correlated $N$-partite state $\rho^{(N)}$, such that the reduced state of each subsystem is $\rho$ and $W_{\text{form}}(\rho^{(N)}) \leq NW_{\text{form}}(\rho)$. Notably, the set of reversible states of Eq. [10] appears naturally in this context, when one considers the set of states that minimizes the corresponding work of formation. Interestingly, if we consider heat engines between these reversible states, it is possible to demonstrate that for large $N$ the efficiency converges to Carnot. As it was shown, the amount of correlations present in these states scales as $O(\log N)$. 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 (see Supplementary Material).

Furthermore, 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.

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 mimes 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. A 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 are allowed a non-zero average work can be extracted at finite efficiency. Here we showed that deterministic work extraction with fixed Hamiltonian requieres strokes with non-equilibrium states. In Fig. 3 (b) we plot the efficiency $\eta^*$ 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 that is extracted during the thermalization stroke. Finally, in \[ \\text{[52, 53]} \] it was shown that no deterministic heat engine exists if the cold bath has finite size. This is an interesting approach while 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.

We have introduced thermodynamic cycles that allow deterministic work extraction in the single-shot regime. While previous work seem to suggest that it is not possible to define such an engine, here we show some general deterministic cycles working with equilibrium and non-equilibrium states. 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 \( T_{\text{hot}} \) and \( A \rightarrow D \) at \( T_{\text{cold}} \)) is enough. We have also show 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 non-equilibrium free energy of the reduced system (which can be chosen arbitrarily).

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**Properties of reversible states**

**Proof.** (Proposition in the main text). We will start by showing that any state has has a thermal-like distribution over a reduced support is reversible. Notice that all the non-zero eigenvalues $\lambda_{E,g}$ of the states $\sigma$ of the form (9) satisfy $\lambda_{E,g} e^{\beta E} = 1/Z$. Then,

$$W_{\text{form}}(\sigma) = \beta^{-1} \log \max_{E,g} \lambda_{E,g} e^{\beta E} - F(\tau(\beta))$$

$$= -\beta^{-1} \log Z - F(\tau(\beta))$$

$$= -\beta^{-1} \log \sum_{E} \dim(\mathcal{U}_E) e^{-\beta E} - F(\tau(\beta))$$

$$= W_{\text{ext}}(\sigma),$$

(11)

which shows that $\sigma$ is a reversible state.

Let us prove now that all reversible states have the form (9). Consider $\rho$ a reversible state and $\text{supp}(\rho)$, with

$$\text{supp}(\rho) = \bigoplus_{E} \mathbf{U}_E^\rho,$$

(12)

where $\mathbf{U}_E^\rho = \text{supp}(\rho) \cap \{|\psi\rangle : H |\psi\rangle = E |\psi\rangle\}$. Let’s define the thermal-like state $\sigma$ on the support of $\rho$, that is,

$$\sigma = \frac{1}{Z_\sigma} \sum_{E} e^{-\beta E} \Pi_{\mathbf{U}_E^\rho}.$$

(13)

Since $\rho$ and $\sigma$ have the same support, they have the same extractable work, $W_{\text{ext}}(\sigma) = W_{\text{ext}}(\rho)$. Now both states are reversible ($\rho$ by hypothesis and $\sigma$ we have proven); therefore

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

(14)

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

$$\max_{E,g} \lambda_{E,g}^\rho e^{\beta E} = \max_{E,g} \lambda_{E,g}^\sigma e^{\beta E} = \frac{1}{Z_\sigma},$$

(15)

where $\lambda_{E,g}^\rho$, $\lambda_{E,g}^\sigma$ are the eigenvalues of $\rho$ and $\sigma$ 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

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

(16)

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

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

$$F(\sigma) = -k_B T \log \sum_{E} \dim(\mathcal{U}_E) e^{-\beta E}. $$

(17)
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 $\rho$ with support $\text{supp}(\sigma)$ 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 $\rho$ thermo-majorizes $\sigma$. Now, given that both states have the same support, the thermo-majorization condition is the same as that for two full-rank probability vectors with the same distribution $\rho$ and $\sigma$ have over $\text{supp}(\sigma)$. Within this subspace $\sigma$ has a thermal distribution and therefore it is majorized by any vector with the same support, in particular $\rho$.

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

In light of these properties, if we have the system initially in an arbitrary non-equilibrium state $\rho$ with non full support, we can always transform it to the reversible state, $\tau|_{U_{\rho}}$, with same support $U_{\rho}$. 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 an non-equilibrium reversible state (i.e. not a thermal state).

**Correlated subsystems**

Consider a working medium of $N$ non-interacting identical qubits. If the gap of the qubits is $\hbar \omega$, then the $N$ qubit system will have an energy spectrum $\{E_m = m\hbar \omega, m = 0, \ldots, N\}$, 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 $\{|0\rangle, |1\rangle\}$ are an orthonormal basis such that $H = \hbar \omega |1\rangle\langle 1|$. In [53] it was shown when such global states $\rho^{(N)}$ of the $N$ qubits with correlations are allowed, then one can have a global work cost of formation lower than that of the uncorrelated subsystems, that is

$$W_{\text{form}}(\rho^{(N)}) < W_{\text{form}}(\rho^{\otimes N}) = N W_{\text{form}}(\rho).$$

In particular, for certain single qubit states $\rho$, the correlated state $\rho^{(N)}$ that minimizes $W_{\text{form}}(\rho^{(N)})$ is a reversible state. This happens for example for local single-qubit states $\rho_k = p_k |1\rangle\langle 1| + (1 - p_k)|0\rangle\langle 0|$, $k = 1, \ldots, N - 1$, such that

$$p_k = \frac{\binom{N}{m}}{\sum_{m=0}^{N} \binom{N}{m} e^{-m \beta \hbar \omega}}.$$  

The respective reversible correlated $N$ qubit states have a Gibbs-like thermal distribution over the support $U_k = \{|E = m\hbar \omega, g\}, g = 1, \ldots, g(m); m = 0, \ldots, k\}$. All relevant thermodynamic quantities of these states are determined by the effective partition function $Z_k(\beta)$ given by

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

For the large $N$ limit that we will be taking later on, it is useful to rewrite this partition function as

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

where $p_\beta = e^{-\beta \hbar \omega} / (1 + e^{-\beta \hbar \omega})$ is the excited state probability of a single qubit in thermal equilibrium and $Z(\beta) = 1 + e^{-\beta \hbar \omega}$ its respective partition function. Notice that the second term in (21) is a tail sum of a binomial distribution characterized by $N$ trials with success probability $p_\beta$. 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

$$B(p_\beta, k_N, N) = \sum_{m=0}^{k_N} \binom{N}{m} p^m_\beta (1 - p_\beta)^{N-m},$$

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

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

and the convergence rate is $O(\log N/N)$. Applying this results to the logarithm of the partition function (21) of the reversible state we have the asymptotic behaviour

$$- \frac{1}{N} \log Z_k(\beta) \approx - \log Z(\beta) + D(q||p_\beta).$$
Therefore, the average energy per qubit is
\[
\frac{1}{N} \langle E \rangle_k = -\frac{1}{N} \frac{\partial}{\partial \beta} \log Z_k(\beta)
\]
\[
\approx p_\beta \hbar \omega + \frac{\partial}{\partial \beta} D(q \| p_\beta)
\]
\[
= p_\beta \hbar \omega + q \hbar \omega - p_\beta \hbar \omega = q \hbar \omega.
\] (25)

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 \( p_k \to q \), 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
\[
F_k(\beta) = NF(q, \beta) + O(\log N),
\] (27)

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 show 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, \( \beta_{\text{hot}} \) and \( \beta_{\text{cold}} \), and different supports \( \mathcal{U} \) and \( \mathcal{V} \) for each number of subsystems \( N \). If we choose our sequence of supports \( \mathcal{U}_{k,v} \) and \( \mathcal{V}_{l,v} \) such that \( k_N/N \to q \) and \( l_N/N \to r \) 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
\[
\frac{W_{\text{cycle}}}{N} \approx F(q, \beta_{\text{hot}}) - F(r, \beta_{\text{hot}}) - F(q, \beta_{\text{cold}}) + F(r, \beta_{\text{cold}}),
\] (28)

so that we simply extract the free energy difference of the local states. Notice that this local states have full support and therefore it would be impossible to deterministically extract any energy from them without the correlations. Furthermore, notice that in the large \( N \) limit we have that the average energy per particle [25] 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 would imply that we have Carnot efficiency. Indeed it is simple to check via direct substitution of the above asymptotic expressions that
\[
\lim_{N \to \infty} \eta = \eta_{\text{Carnot}}.
\] (29)