Extractable Work from Correlations

Martí Perarnau-Llobet,[1] Karen V. Hovhannisyan,[1] Marcus Huber,[2,1] Paul Skrzypczyk,[1,3] Nicolas Brunner,[4] and Antonio Acín[1,5]

[1]*ICFO-Institut de Ciencies Fotoniques, Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain*
[2]*Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain*
[3]*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*
[4]*Département de Physique Théorique, Université de Genève, 1211 Genève, Switzerland*
[5]*ICREA-Institució Catalana de Recerca i Estudis Avançats, Lluis Companys 23, 08010 Barcelona, Spain*

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Work and quantum correlations are two fundamental resources in thermodynamics and quantum information theory. In this work, we study how to use correlations among quantum systems to optimally store work. We analyze this question for isolated quantum ensembles, where the work can be naturally divided into two contributions: a local contribution from each system and a global contribution originating from correlations among systems. We focus on the latter and consider quantum systems that are locally thermal, thus from which any extractable work can only come from correlations. We compute the maximum extractable work for general entangled states, separable states, and states with fixed entropy. Our results show that while entanglement gives an advantage for small quantum ensembles, this gain vanishes for a large number of systems.

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I. INTRODUCTION

Traditional, macroscopic thermodynamics is strikingly robust to the underlying mechanics: its three laws hold true while switching from classical to quantum mechanics [1]. On the other hand, one would hope for the opposite, since thermodynamics is intimately connected to information theory [2], and quantum phenomena, such as entanglement, have a drastic effect on the latter, irrespective of the scale [3].

Recently, much attention has been dedicated to the problem of understanding thermodynamics of small quantum systems. This has led notably to the development of a resource theoretical formulation of quantum thermodynamics [4–6] and, in a more practical vein, to the study of quantum thermal machines [7–15]. The role and significance of quantum effects to thermodynamics is still to be fully understood, although progress has recently been made [13–22].

A problem of particular importance in quantum thermodynamics is to understand which quantum states allow for the storage and extraction of work from quantum systems [23,24]. Such states are called nonpassive, while states from which no work can be extracted are referred to as passive. Remarkably, the latter have the property of activation: when considered as a whole, several copies of passive states can become nonpassive. The only states lacking this property are the thermal (also referred to as completely passive) states [23,24].

The situation changes when considering ensembles that can also be correlated. There, even a collection of locally thermal states can be nonpassive [25–27]. The main goal of the present work is to understand how to optimally make use of correlations among quantum systems for work storage. Specifically, we consider a quantum ensemble composed of n subsystems (particles or modes). Each subsystem is assumed to be in a thermal state, at the same temperature T. The total system, however, is correlated, because otherwise its state would also be thermal, hence, passive. This is in fact the natural scenario to study the role of correlations for work storage, as they become the only source of nonpassivity.

First, we show that if no restriction on the global state is made, then it is possible to store in the system the maximal amount of work compatible with the requirement that the reduced states are thermal. In other words, at the end of the protocol, the system is left in the ground state and, thus, all energy has been extracted. Notably, this is possible thanks to quantum entanglement. It is then natural to ask if the same amount of work can be stored using a separable or even a purely classical state diagonal in the product energy eigenbasis, that is, with no coherences among different

energy levels. We show that, although the amount of work that can be stored in unentangled states is strictly smaller than the amount that can be stored in entangled states for any finite n, the gain decreases with the size of the system and in the thermodynamic limit ($n \to \infty$) purely classical states already become optimal. In fact, quantum resources offer a significant advantage only for small n, while neither entanglement nor energy coherences are needed for optimal work storage in the thermodynamic limit. We also consider additional natural constraints on the global state, such as limiting the entropy or requiring the decohered (classical) version of the state to be thermal, and investigate the role of quantum coherence and entanglement in these cases.

Finally, we show that our results are also applicable in the scenario where the system has access to a thermal bath. There, the connection between work extraction and correlations has been studied before [11,19,28–35]. Given access to global operations on the subsystems, the extractable work is proportional to the mutual information [28,31]. That is, only the strength of the correlations is relevant, and not the type (i.e., quantum or classical). Here, in contrast, we show that when the bath (a macroscopic object) is not available and one has only a few subsystems, quantum correlations do provide a sizable advantage. This brings new insights in the quantum-to-classical transition in thermodynamics.

II. FRAMEWORK

We consider an isolated quantum system that consists of n d-level subsystems. The local Hamiltonian $h = \sum_a E_a|a\rangle\langle a|$ is taken to be the same for each subsystem and, without loss of generality, it is assumed that the ground state energy is zero. We consider the situation where there is no interaction Hamiltonian between the subsystems, such that the total Hamiltonian H is simply the sum of the individual local Hamiltonians, $H = \sum_i h_i$.

The class of operations that we consider is the class of cyclic Hamiltonian processes;, i.e., we can apply any time-dependent interaction $V(t)$ between the n subsystems for a time τ, such that $V(t)$ is nonvanishing only when $0 \le t \le \tau$. The corresponding evolution can be described by a unitary operator, $U(\tau) = \overrightarrow{\exp}\{-i \int_0^\tau dt[H + V(t)]\}$, where $\overrightarrow{\exp}$ denotes the time-ordered exponential. By varying over all $V(t)$, we can generate any unitary operator $U = U(\tau)$, and, therefore, this class of operations can alternatively been seen as the ability to apply any global unitary on the system.

The task we are interested in is work extraction via a cyclic Hamiltonian process. Since the system is taken to be isolated, there are no other systems to exchange energy with; therefore, the extracted work is the change in average energy of the system under such a process [36]. More precisely, we define the extracted work W as

$$W = \mathrm{Tr}(\rho H) - \mathrm{Tr}(U\rho U^\dagger H). \tag{1}$$

Within this framework, it is well known that work can be extracted from a system if and only if the system is *nonpassive*, where a passive system with Hamiltonian $H = \sum_\alpha \mathcal{E}_\alpha|\alpha\rangle\langle\alpha|$ ($\mathcal{E}_\alpha \le \mathcal{E}_{\alpha+1}$) is the one whose state is of the form

$$\rho^{\mathrm{passive}} = \sum_\alpha p_\alpha|\alpha\rangle\langle\alpha|, \quad \text{with} \quad p_{\alpha+1} \le p_\alpha. \tag{2}$$

In other words, a system is passive if and only if its state is diagonal in the energy eigenbasis and has eigenvalues nonincreasing with respect to energy. Now it easily follows that, given a nonpassive state ρ, the extracted work (1) is maximized by [37]

$$W_{\max} = \mathrm{Tr}(\rho H) - \mathrm{Tr}(\rho^{\mathrm{passive}} H), \tag{3}$$

where ρ and ρ^{passive} have the same spectrum and therefore there exists a unitary operator taking the former to the latter. Equation (3) defines the energy that can be potentially extracted from the state via cyclic Hamiltonian (unitary) processes. This quantity is the main focus of this article, and we refer to it as extractable work, stored work, or work content (the term *ergotropy* is also used in the literature [37]).

Importantly, we see that passivity is a global property of a system, and thus this raises interesting possibilities when considering a system composed of a number of subsystems, as we do here. Indeed, global operations are capable of extracting more work than local ones, as a state can be locally passive but globally not. Such an enhancing may have two origins: activation or correlations between subsytems. Activation occurs when $(\rho^{\mathrm{passive}})^{\otimes k}$ becomes a nonpassive state for some k. Interestingly, thermal states are the only passive states that do not allow for activation, as any number of copies of thermal states is also thermal [23,24]. On the other hand, states that are locally passive but have a nonproduct structure (i.e., they are correlated) also offer the possibility for work extraction. An extreme case, which is the focus of this article, is a set of correlated locally thermal states, as in such a case the global contribution uniquely comes from correlations. Our goal, in fact, is to understand how correlations allow for work extraction in systems that are locally completely passive [38].

We therefore focus on the subset of all possible states of the system, comprised by locally thermal states, that is, all ρ such that the reduced state of subsystem i satisfies

$$\rho_i = \mathrm{Tr}_{\bar{i}}\rho = \tau_\beta \tag{4}$$

for all i, where $\mathrm{Tr}_{\bar{i}}$ denotes the partial trace over all subsystems except subsystem i. Here, τ_β is the thermal state of the subsystem at (a fixed but arbitrary) inverse temperature $\beta = 1/T$,

$$\tau_\beta = \frac{1}{\mathcal{Z}} e^{-\beta h}, \tag{5}$$

where $\mathcal{Z} = \mathrm{Tr} e^{-\beta h}$ is the partition function.

Now, if ρ is locally thermal [Eq. (4)], and since H is a sum of local Hamiltonians, the first term on the right-hand side of Eq. (3) is fixed and is given by $\mathrm{Tr}(\rho H) = nE_\beta$, where $E_\beta = \mathrm{Tr}(\tau_\beta h)$ is the average energy of the local thermal state. Note also that given our convention that the ground state has zero energy, the second term on the right-hand side of Eq. (3), that is, the final average energy, is always non-negative. This implies that the extractable work is upper bounded by

$$W_{\max} \leq nE_\beta. \tag{6}$$

This bound is attainable if and only if the final state is the ground state, denoted by $|0\rangle^{\otimes n}$.

Apart from understanding how to exploit the general correlations to store work in the system, we also study the particular role of entanglement and energy coherences in these processes. We consider three natural sets of correlated states: (i) arbitrary states, thus including entangled ones, (ii) separable states and a subset of them, and (iii) states diagonal in the product energy eigenbasis. We study work extraction for these three different sets of correlated quantum states.

Before proceeding further, we end by noting that in the present context our quantity of interest is the *average* extractable work. This allows us to obtain precise and quantitative results about the relation between work and quantum correlations in the initial state. The question of how to obtain similar results, for example, about the full work probability distribution, in general remains a difficult open problem. Essentially, at the moment there is no framework allowing us to obtain the full work distribution function of the process without destroying the initial coherences (and entanglement) of the state (see Ref. [39] for a discussion on how to extend fluctuation theorems for coherent states).

III. EXTRACTABLE WORK FROM CORRELATIONS

We first show that within the above framework quantum correlations are capable of making all the energy in the system available for extraction in the form of work, as they allow saturating the bound [Eq. (6)]. As mentioned above, it can only be saturated if and only if $U\rho U^\dagger$ is the ground state. Now, observe that the state

$$|\phi\rangle = \frac{1}{\sqrt{\mathcal{Z}}} \sum_{a=0}^{d-1} e^{-\beta E_a/2} |a\rangle^{\otimes n} \tag{7}$$

is locally thermal, i.e., such that $\mathrm{Tr}_{\bar{i}}|\phi\rangle\langle\phi| = \tau_\beta$ for all i. Moreover, since it is pure, there exists a unitary matrix U such that $U|\phi\rangle = |0\rangle^{\otimes n}$. Thus, all the energy nE_β can be extracted from state $|\phi\rangle$ and $W_{\max} = nE_\beta$.

However, it is clear that the state Eq. (7) is entangled. Hence, it is natural to ask whether the amount of extractable work would change if we restrict ourselves to separable, or even classical, states. If this is the case, then entanglement is necessary for optimal work extraction.

IV. EXTRACTABLE WORK FROM SEPARABLE AND CLASSICAL STATES

A simple argument shows that separable states, contrary to entangled, do not allow for maximal work extraction. Separable states have the property that the global entropy is greater than all the local entropies [40]. Now, if the system is initially in a separable state ρ, then $S(\rho) \geq S(\tau_\beta)$. This condition, first of all, indicates that the global state cannot be pure [41], implying that the bound Eq. (6) cannot be reached by separable states. So, what is the best that classical correlations can do?.

In Appendix A, we show that the locally thermal separable state with the highest extractable work is

$$\rho_{\mathrm{sep}} = \frac{1}{\mathcal{Z}} \sum_{a=0}^{d-1} e^{-\beta E_a} |a\rangle\langle a|^{\otimes n}, \tag{8}$$

which is simply the state Eq. (7) after being dephased in the (global) energy eigenbasis. Notice that Eq. (8) saturates the inequality $S(\rho) \geq S(\tau_\beta(h))$, and in Appendix A 2, we show that it is the only separable state with thermal reduced states that saturates it. The extractable work from Eq. (8), W_{sep}, is found, as before, by finding its associated passive state, and then computing the average energy difference; see Eq. (3). Since ρ_{sep} is already diagonal (with d nonzero eigenvalues), it is only necessary to rearrange these nonzero eigenvalues to the lowest possible energy levels. Let us assume that $n \geq d-1$ (i.e., that we are in the regime of sufficiently many subsystems [42]). The $d-1$ largest eigenvalues can then simply be moved into the first excited subspace (with energy E_1), giving

$$W_{\mathrm{sep}} = nE_\beta - E_1(1 - \mathcal{Z}^{-1}). \tag{9}$$

Note also that ρ_{sep} has no coherences, which means that diagonal and separable states have the same capacity.

Moreover, as the number of subsystems n increases, we see that W_{sep} and $W_{\max}$ become essentially the same: $W_{\mathrm{sep}}/W_{\max} = 1 - \mathcal{O}(n^{-1})$ (see Fig. 1). This shows that, in the thermodynamic limit ($n \to \infty$), the difference between the extractable work from an entangled state and from a diagonal one vanishes; hence, quantum coherences and entanglement play essentially no role here. However, for finite n there will always be a difference. In particular, in the regime of n relatively small, the ability

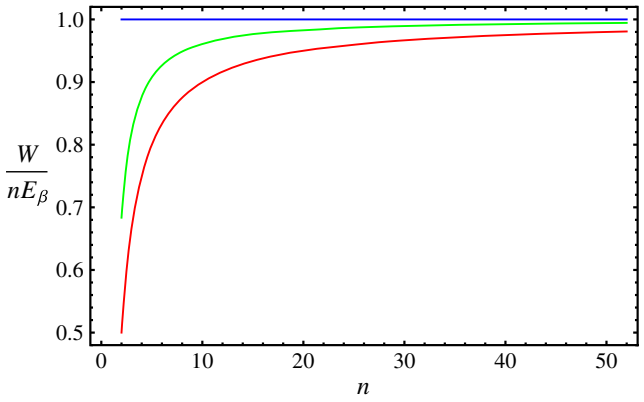

FIG. 1. Extractable work from entangled (blue line), separable (red line), and entangled but having the same entropy as the separable (green line) states in units of the initial total energy of the system. Specifically, we take the states Eqs. (7), (8), and (11) for $d = 2$, $\beta E_1 = 1$. As n increases, classical states become able to store essentially the same amount of work as quantum ones.

to store work in entanglement offers a significant advantage (see Fig. 1).

At this point, let us note that for diagonal initial states [such as Eq. (8)], the (average) extractable work as given by the definition Eq. (1) coincides with the first moment of work distribution functions introduced in Refs. [43,44].

V. EXTRACTABLE WORK FROM STATES WITH FIXED ENTROPY

The previous results can be intuitively understood from entropy considerations. When the correlations in the state are not restricted, it is possible to satisfy the requirement of local thermality with pure entangled states, therefore attaining optimal work extraction. When the state is separable, the global entropy of the state cannot be zero as it is lower bounded by the local entropy and optimal work extraction becomes impossible. Note also that the separable state optimal for work extraction [Eq. (9)] has global entropy equal to the local one, which means that its global entropy does not scale with the number of subsystems. In other words, its entropy per subsystem tends to zero with the number of subsystems, which intuitively explains why the state tends to be optimal in this limit.

In view of these considerations, it is important to understand how one can store work in correlations when the entropy of the state is fixed. On the one hand, having states whose global entropy scales with the number of subsystems seems more realistic. On the other hand, this allows a more fair comparison between entangled and separable states. In this section, we show that quantum coherences and entanglement enhance the work storage capacity even if the entropy of the global state is fixed. This implies that the entropy gap between separable and entangled states mentioned above is not the only factor making classical states generically worse. However, as in the case of nonrestricted entropy, the gain provided by entangled states or energy coherences vanishes in the thermodynamic limit.

Stated otherwise, the question is whether locally thermal quantum states subject to the constraint $S(\rho) = S$ can store more work than Eq. (9) when $S = S(\tau_\beta)$. Now, keeping in mind that local thermality fixes the initial energy to be nE_β, finding the extractable work $W_{\max}(S)$ amounts to minimizing the final energy $\mathrm{Tr}(H\sigma)$ over all $\sigma = U\rho U^\dagger$, with U being unitary and ρ satisfying the conditions above.

One can readily lower bound $\mathrm{Tr}(H\sigma)$ by relaxing all the constraints except $S(\sigma) = S$. Then, as is well known from standard statistical mechanics, the state with the least energy compatible with a given entropy is the thermal state [23,24]

$$\rho_{\mathrm{th}} = \tau_{\beta'}^{\otimes n}, \tag{10}$$

with $\beta' = \beta'(S)$ being the (unique) [45] solution of the entropy constraint $S(\tau_{\beta'}) = S/n$. So, $\mathrm{Tr}(H\sigma) \geq \mathrm{Tr}(H\rho_{\mathrm{th}}) = n\mathrm{Tr}(h\tau_{\beta'})$. This implies a bound on the extractable work:

$$W_{\max}(S) \leq nE_\beta\left(1 - \frac{1}{E_\beta}\mathrm{Tr}(\tau_{\beta'}h)\right). \tag{11}$$

In principle, it is not clear if the previous bound is attainable, as the way we find ρ_{th} does not guarantee it to be unitarily achievable from any of the allowed initial states. Nevertheless, as we show below, for any given S and any number n of qubits [46] there always exists a locally thermal quantum state that can be transformed to ρ_{th} by a suitable unitary operator; i.e., the bound Eq. (11) is tight.

Before moving to explicit protocols, let us show a direct consequence of the bound Eq. (11). As the maximal extractable work from separable states, given in Eq. (9), is obtained for $S = S(\tau_\beta)$, one can easily compare it to $W_{\max}[S(\tau_\beta)]$. The result is illustrated in Fig. 1, showing that $W_{\mathrm{sep}} < W_{\max}[S(\tau_\beta)]$. Therefore, even if the entropy is fixed, classical states are generically weaker than entangled quantum states in terms of work storage as the states delivering $W_{\max}[S(\tau_\beta)]$ are necessarily entangled. To understand the reason for this difference, notice that the separability condition restricts the set of locally thermal states (see Appendix A 2), thereby limiting their possible spectra, which, in turn, determine [according to Eq. (3)] the extractable work.

Now, let us show an explicit protocol that delivers Eq. (11). Since to reach the bound in Eq. (11) the system has to necessarily end up in the state Eq. (10), we, for clarity, construct the backwards unitary, which takes the final state $\tau_{\beta'}^{\otimes n}$ to an initial state ρ which is locally thermal, at any temperature $\beta \leq \beta'$. In what follows. it is convenient to introduce the local parameter $z = \langle 0|\tau_\beta|0\rangle - \langle 1|\tau_\beta|1\rangle$, i.e., the "bias" of the local (qubit) subsystem in state τ_β. It is a monotonic function of the temperature: $z = \tanh(\beta E/2)$

(from now on, we concentrate on qubits and, therefore, drop the index of E_1).

We first consider the simplest case of two qubits. Define the unitary transformation U_α to be a rotation by an angle α,

$$\begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix},$$

in $\{|00\rangle, |11\rangle\}$ (the subspace spanned by $|00\rangle$ and $|11\rangle$) and an identity on the rest of the space.

If as an initial state we take $\rho = U_\alpha \tau_{\beta'}^{\otimes 2} U_\alpha^\dagger$, then since U_α only generates coherences in the subspace where both qubits are flipped, it is clear that the reduced state of each qubit is diagonal. A straightforward calculation shows that under the action of U_α, the state $\tau_{\beta'}$ (with bias z') transforms to an initial state ρ with bias $z = \cos(2\alpha)z'$. That is, we can achieve any bias z such that $|z| \leq z'$. As such, the local temperature of the initial state, which is simply given by $\beta = (2/E)\tanh^{-1}[\cos(2\alpha)z']$, can take any temperature $\beta \leq \beta'$ by an appropriate choice of α.

The above protocol can be readily generalized to the case of n qubits. Let us denote by $\mathbf{i} = i_1, \ldots, i_n$ an n-bit string, with $|\mathbf{i}| = \sum_k i_k$ being the Hamming weight (number of 1's) of the string. The states $|\mathbf{i}\rangle = |i_1\rangle \ldots |i_n\rangle$ run over all 2^n energy eigenstates of H. We also introduce $\bar{\mathbf{i}}$—the bit-wise negation of $\mathbf{i}$ (i.e., $|\bar{\mathbf{i}}\rangle = \sigma_x^{\otimes n}|\mathbf{i}\rangle$). As we show in Appendix B, if we now apply an U_α in each of the subspaces $\{|\mathbf{i}\rangle, |\bar{\mathbf{i}}\rangle\}$ with $0 \leq |\mathbf{i}| < n/2$ [47], the resulting state is locally thermal, and, exactly as in the case of two qubits, the local bias z is given by $z = \cos(2\alpha)z'$. Again, any bias $|z| \leq z'$ and therefore any temperature $\beta \leq \beta'$ can be reached.

Notice that the protocol exploits coherence in all two-dimensional subspaces spanned by $|\mathbf{i}\rangle$ and $|\bar{\mathbf{i}}\rangle$. We expect these optimal states to be entangled in general, and, in fact, they are entangled for the scenario depicted in Fig. 1. Moreover, we can also show that in the limit of large n the optimal states are necessarily entangled (see Appendix B 1).

Despite this result, in the thermodynamic limit, the bound Eq. (11) can always be asymptotically reached by (purely classical) diagonal states. To prove this, we distinguish two qualitatively different situations of the global entropy S being macroscopic ($S \propto n$) and submacroscopic ($S/n \to 0$). In the latter case, as is detailed in Appendix B 2, the proof is conducted by analyzing a generalized version of the state Eq. (8), whereas the former case of macroscopic entropy can be treated by a simple adaptation of the above protocol. Specifically, as the final state one chooses $\rho_{\text{th}} = \tau_{\beta'}^{\otimes n}$, with $S(\tau_{\beta'}) = \lim_{n\to\infty} S/n$ and, by applying $U_{\frac{\pi}{2}}$, inverts the populations in one subspace $\{|\mathbf{i}\rangle, |\bar{\mathbf{i}}\rangle\}$ with $|\mathbf{i}| = k \simeq n e^{-\beta' E}/\mathcal{Z}'$. This changes the bias from z' to $z' - \mathcal{O}(1/\sqrt{n})$. So, by performing $\mathcal{O}(\sqrt{n})$ population inversions, one can approximate any $|z| < z'$ and, hence, any temperature $\beta < \beta'$ (see Appendix B 3 for details).

By running the above protocol backwards, one immediately notices that the work extraction from correlations is related to the process of their creation from a product of thermal states. In fact, the problem of correlating the latter states as much as possible for a given amount of invested work is considered in Refs. [48,49]. There, it is shown that the process is optimal when the final state is locally thermal, which is our starting point here. On the other hand, work extraction becomes optimal when the final state is (globally) thermal. That is, the two processes become the reverse of each other *only* when they are both optimal. This situation is in fact common in thermodynamics. For example, a heat engine working at Carnot efficiency can be seen as an optimal refrigerator running backwards [1].

VI. EXTENSION TO OTHER SCENARIOS

Before concluding, we show how our techniques can be applied to other relevant scenarios again in the context of optimal work storage in correlations. In particular, we consider systems where (i) all moments of the energy distribution are equal to those of a global thermal state and (ii) one has access to a thermal bath.

A. Work from energy coherences

We first consider states whose diagonal (in the energy eigenbasis) is set to be equal to that of a global thermal state, together with the initial condition of local thermality. More formally, this approach is equivalent to imposing that all moments of the energy distribution are those of the global thermal state: $\text{Tr}(H^k\rho) = \text{Tr}(H^k\tau_\beta^{\otimes n})$, for all k. This contrasts with the previous sections where only the first moment (i.e., the average energy) is fixed by local thermality. Moreover, notice that the entropy of the initial state is here unconstrained.

Focusing again first on the case of n qubits, we consider states that are maximally entangled in every degenerate subspace:

$$\rho_{\text{deg}} = \sum_{k=0}^{n} C_n^k p^k (1-p)^{n-k} |D_{n,k}\rangle\langle D_{n,k}|, \qquad (12)$$

where $p = e^{-\beta E}/\mathcal{Z}$, and $|D_{n,k}\rangle \propto \sum_{|\mathbf{i}|=k} |\mathbf{i}\rangle$ is the normalized Dicke state of n qubits with k excitations. It is straightforward to verify that the above state satisfies Eq. (4) and has the required diagonal elements.

The passive state associated with Eq. (12) is found as follows. Notice that the state Eq. (12) is a mixture of $n+1$ orthogonal states. Therefore, the optimal unitary amounts to rotating each of these states to the $n+1$ lowest energy levels, one of which is the ground state with zero energy and the other n have energy E. Therefore, the energy of the transformed state is smaller than E, which means that it is possible to extract all the energy contained in the initial state up to a correction of $\mathcal{O}(1)$:

$$W_{\mathrm{deg}} = nE_\beta - \mathcal{O}(1)E. \tag{13}$$

A similar result holds for the general case of n qudits (see Appendix C).

An interesting question is whether the state ρ_{deg} features entanglement. Intuition suggests that this may be the case, as large coherences are crucial in this scenario. However, using the techniques developed in Ref. [50], we have not been able to witness entanglement for $n \leq 50$. Based on this evidence, it seems that in this case entanglement may not provide an advantage for any number of subsystems.

B. Access to a bath

Finally, we consider an extended scenario in which the system is no longer isolated and can be put in contact with a bath at the same (local) temperature. Here, we ask what is the maximal work that can be extracted via unitaries acting jointly on the system and the bath. Then it is well known that the extractable work is upper bounded by the difference between initial and thermal free energies:

$$W_{\mathrm{max}} \leq F[\rho] - F[\tau_\beta^{\otimes n}], \tag{14}$$

where $F[\rho] = \mathrm{Tr}(H\rho) - \beta^{-1}S(\rho)$ and the inequality can be saturated (e.g., via infinitely slow isothermal processes [51]) [1,44,52,53].

In the present case, the extractable work from any locally thermal state with entropy S is given by

$$W_{\beta,\mathrm{max}}(S) = \beta^{-1}[nS(\tau_\beta) - S], \tag{15}$$

where the expression in square brackets is nothing other than a multipartite generalization of the quantum mutual information. This enforces our argument that the origin of the extractable work is the correlations in the state. The bound Eq. (15) is strictly bigger than Eq. (11), which is natural, as we consider a larger set of operations. On the other hand, the states Eqs. (7) and (8) maximize the right-hand side of Eq. (15), i.e., the free-energy content is maximal, for entangled and separable states, respectively, and thus our previous considerations also hold in this framework.

For the case of extracting work from energy coherences, one can readily use Eq. (15) by computing the entropy of Eq. (12). As ρ_{deg} is a mixture of $n+1$ pure states, its entropy cannot exceed (and, as can easily be shown, actually scales as) $\ln(n+1)$. Therefore, ρ_{deg} allows for storing all work in coherences except for a $\mathcal{O}(\ln n)$ correcting term. We note that this optimal state cannot be expressed as a tensor product of many coherent states, a situation that was considered previously in the literature [4,44].

Notice that, when given access to a bath, the extractable work depends only on a single global property, namely, the free energy of the state, which here reduces to the generalized mutual information [Eq. (15)]. Therefore, the strength of the correlations becomes the only important property, and not whether they are quantum or not. This is in contrast to our previous results in Sec. V. In order to reconcile both results, imagine that a bath at temperature β' is attached to our system. Then, the bound Eq. (14) (with β substituted by β') will reduce exactly to Eq. (11). Therefore, we see that separable states can saturate Eq. (11) when a macroscopic object, i.e., a bath, is available. This corroborates our result in Sec. V, namely, that in the thermodynamic limit [54] the difference between quantum and classical correlations vanishes.

Our results in this section thus complement a previous study [32] in a similar setting, and also the works [19,28–31,33,55], which, although in a completely different context, also deal with the problem of work extraction from thermal environments utilizing correlations. Finally, it is worth mentioning that when the correlations are not present between subsystems but rather between the system and the bath, they become a source of irreversibility [16].

VII. CONCLUSIONS

In this work, we investigate and compare the work storing capacities of quantum and classical correlations. To eliminate all sources of work except correlations, we consider systems that are locally thermal. The latter condition is both necessary and sufficient to ensure that the system becomes passive once the correlations are removed. This gives a new perspective on the problem of passivity, in particular, for the case of composite systems.

We first show that correlations are powerful enough to allow for the extractable work to be equal to all the energy present in the system (see Sec. III). For that to happen, the state of the system must not only be entangled but also pure, which is impossible for locally thermal separable states due to an entropy constraint. Entanglement is also useful when the state of the system is mixed, as in this case we show that separable states cannot generically store the maximal work compatible with the entropy of the system and local thermality.

Furthermore, we prove that in all cases the quantum advantage, significant for small ensembles, becomes irrelevant in the thermodynamic limit, thereby corroborating that macroscopic thermodynamics is insensitive to the microscopic mechanics underlying it. This "classical" view is complemented by a previous result by some of us [18] stating that maximal work can be extracted from diagonal states without generating entanglement during the whole process.

The considered scenario, a set of correlated yet locally thermal states, is ideal to identify the role of quantum effects in thermodynamics and naturally allows for extensions. In this respect, first, we study the role of coherences

by further restricting the diagonal of the state in the energy eigenbasis to be identical to a thermal state. Interestingly, in this case it turns out that, in the thermodynamic limit, essentially all the energy can be stored in the off-diagonal terms. Secondly, we discuss the situation when the system is allowed to interact with a thermal bath at the local temperature of the reduced states. Then, work is directly related to the strength of the correlations as measured by Eq. (15).

An interesting open question is to investigate the scenario in which not only local marginals are thermal, but so are k-body reduced states (in particular, the case of nearest neighbors). This may give an insight into the role of different types of multipartite entanglement in the context of work extraction. Another interesting question is to derive bounds in the other direction, i.e., correlated states with minimal work content [56]. A promising line of further research is to study the process of converting correlations into work beyond average quantities, for example, from the point of view of fluctuation theorems [43], or deterministic work extraction [53,57,58].

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APPENDIX A: MAXIMAL WORK FROM SEPARABLE STATES

In this Appendix, we find the maximal work that can be stored in separable states subject to being locally thermal.

1. The set

In other words, we want to find the maximum of the ergotropy Eq. (3),

$$W_{\max}(\rho) = \mathrm{Tr}(H\rho) - \mathrm{Tr}(H\rho^{\mathrm{passive}}), \tag{A1}$$

over all those ρ's that belong both to the set of separable states (we denote it as $\mathcal{SEP}$) and to

$$\mathcal{LTH} = \{\rho : \mathrm{Tr}_{\bar{i}}\rho = \tau_\beta, i = 1, \ldots, n\}. \tag{A2}$$

Now observe that, along with $\mathcal{SEP}$ [59], $\mathcal{LTH}$ is a convex set. Indeed, if ρ_1 and ρ_2 are two arbitrary states belonging to $\mathcal{LTH}$, then for $\forall\ t \in [0,1]$,

$$\mathrm{Tr}_{\bar{i}}[t\rho_1 + (1-t)\rho_2] = t\tau_\beta + (1-t)\tau_\beta = \tau_\beta, \tag{A3}$$

for all i, immediately implying that $t\rho_1 + (1-t)\rho_2 \in \mathcal{LTH}$ for all $t \in [0,1]$, which, by definition, means $\mathcal{LTH}$ is a convex set. Moreover, since the conditions defining $\mathcal{LTH}$ are linear, it is also a closed set.

We also need the following set:

$$\mathcal{ENT}(S) = \{\rho : S(\rho) \geq S\}. \tag{A4}$$

Because of convexity of the von Neumann entropy, $\mathcal{ENT}$ is also convex and the non-strict inequality in the definition ensures that it is also closed.

Another observation is that, since the entropy of the separable states is greater than all the local entropies, we have that if $\rho \in \mathcal{SEP} \cap \mathcal{LTH}$, then $S(\rho) \geq S(\tau_\beta)$. Otherwise,

$$\mathcal{SEP} \cap \mathcal{LTH} \subset \mathcal{ENT}(S(\tau_\beta)). \tag{A5}$$

Moreover, the intersection of the boundaries of all three sets in Eq. (A21) is nonempty and consists of only one element, which we find in the next section.

2. Maximally pure separable state

Here, we determine the separable state ρ_{sep} of N systems (all having the same d-level Hamiltonian $h = \sum_{a=0}^{d-1} E_a|a\rangle\langle a|$) such that it has the minimal entropy compatible with marginals all being τ_β (5):

$$\tau_\beta = \frac{1}{Z}e^{-\beta h} = \frac{\sum_{a=0}^{d-1} e^{-\beta E_a}|a\rangle\langle a|}{\sum_{b=0}^{d-1} e^{-\beta E_b}} \equiv \sum_{a=0}^{d-1} p_a|a\rangle\langle a|. \tag{A6}$$

Considering, e.g., the first system (S^1) versus the rest ($R = S^2 \otimes \ldots \otimes S^N$) and keeping in mind that the partial states of S's are all τ_β, we have

$$S(\rho_{\mathrm{sep}}) - S(\tau_\beta) = -S\left(\rho_{\mathrm{sep}} || \tau_\beta \otimes \frac{I_R}{d_R}\right) + \ln d_R. \tag{A7}$$

Since ρ_{sep} is separable, it can be written in the following form:

$$\rho_{\text{sep}} = \sum_x \lambda_x \rho_x^{S^1} \otimes \rho_x^R = \sum_x \lambda_x \rho_x^{S^1} \otimes \rho_x^{S^2} \otimes \ldots \otimes \rho_x^{S^N}, \tag{A8}$$

for some discrete index x, non-negative λ_x's summing up to 1, and some normalized states $\rho_x^{S^i}$ over S^i. Given the condition that the state of S^1, $\sum_x \lambda_x \rho_x^{S^1}$, is equal to τ_β and the joint convexity of the relative entropy [60], we have

$$\begin{aligned} S(\rho_{\text{sep}}) - S(\tau_\beta) &= \ln d_R - S\left(\sum_x \lambda_x \rho_x^{S^1} \otimes \rho_x^R || \sum_x \lambda_x \rho_x^{S^1} \otimes \frac{I_R}{d_R}\right) \\ &\geq \ln d_R - \sum_x \lambda_x S\left(\rho_x^{S^1} \otimes \rho_x^R || \rho_x^{S^1} \otimes \frac{I_R}{d_R}\right) \\ &= \sum_x \lambda_x S(\rho_x^R) \geq 0. \end{aligned} \tag{A9}$$

So, the minimal possible value for $S(\rho_{\text{sep}})$ is $S(\tau_\beta)$; and to find the purest ρ_{sep}, we have to saturate both inequalities in the chain Eq. (A9). The second inequality is resolved trivially, giving that $\rho_x^R = \rho_x^{S^2} \otimes \ldots \otimes \rho_x^{S^N}$ for all values of x are pure. We denote these states as $|R_x\rangle = |S_x^2\rangle \otimes \ldots \otimes |S_x^N\rangle$. Doing the same with respect to, e.g., S^2, we will get that all $\rho_x^{S^1}$ are also pure (and, as above, are denoted as $|S_x^1\rangle$).

The equality conditions for the first inequality of Eq. (A9) are less trivial [60]. If we consider only the nonzero λ_x's and denote their number by L, Theorem 8 of Ref. [60] will give us

$$(\lambda_x \rho_x^{S^1} \otimes \rho_x^R)^{it} \left(\lambda_x \rho_x^{S^1} \otimes \frac{I_R}{d_R}\right)^{-it} = \rho_{\text{sep}}^{it} \left(\tau_\beta \otimes \frac{I_R}{d_R}\right)^{-it} \quad \text{for } \forall\ t > 0 \quad \text{and} \quad x = 0, \ldots, L-1, \tag{A10}$$

where the equality holds in the support of $\rho_x^{S^1} \otimes \rho_x^R = |S_x^1 \ldots S_x^N\rangle\langle S_x^1 \ldots S_x^N| = |S_x\rangle\langle S_x| = P_x$ (in this notation, $\rho_{\text{sep}} = \sum_x \lambda_x P_x$). The latter is the projector onto that subspace. Bearing in mind that we consider only nonzero λ_x's and doing the same procedure for all other $N-1$ systems, we get from Eq. (A10):

$$\begin{aligned} P_x \rho_{\text{sep}} P_x &= P_x(\tau_\beta \otimes I_{S^2} \otimes \ldots \otimes I_{S^N}) P_x = \cdots \\ &= P_x(I_{S^1} \otimes I_{S^2} \otimes \ldots \otimes \tau_\beta) P_x. \end{aligned} \tag{A11}$$

We now concentrate on the first equality and, for simplicity, drop the index enumerating the subsystems. With that, and taking into account that $P_x \rho_{\text{sep}} P_x = \lambda_x P_x$ and $P_x(\tau_\beta \otimes I_{S^2} \otimes \ldots \otimes I_{S^N}) P_x = \langle S_x|\tau_\beta|S_x\rangle P_x$, we have

$$\lambda_x = \langle S_x|\tau_\beta|S_x\rangle. \tag{A12}$$

Now we take $\{|a\rangle\}_{a=0}^{d-1}$, the eigenbasis of τ_β in the Hilbert space of the subsystem Eq. (A6), and construct the matrix $m_{xa} = |\langle S_x|a\rangle|^2 \geq 0$. With this, we rewrite Eq. (A12) as

$$\sum_{a=0}^{d-1} m_{xa} p_a = \lambda_x. \tag{A13}$$

Also, from the normalization, we have

$$\sum_a m_{xa} = 1 \quad \text{for } \forall\ x. \tag{A14}$$

Finally, the condition that all partial states are τ_β: $\sum_x \lambda_x |S_x\rangle\langle S_x| = \tau_\beta$ leads us to

$$\sum_{x=0}^{L-1} \lambda_x m_{xa} = p_a. \tag{A15}$$

First, let us show that $L > d$ cannot be true. Indeed, substitute Eq. (A13) into Eq. (A15), $\sum_{xb} m_{xa} m_{xb} p_b = p_a$, multiply the lhs by m_{xa} and sum over a and use $\sum_x \lambda_x = 1 = \sum_{xa} m_{xa} p_a$:

$$\sum_x \left(\sum_a m_{xa}^2\right)\left(\sum_b m_{xb} p_b\right) = 1. \tag{A16}$$

Given that it must hold that $\sum_{xa} m_{xa} p_a = 1$, we see that Eq. [(A16)] can be true only if

$$\sum_a m_{xa}^2 = 1 \quad \text{for } \forall\ x. \tag{A17}$$

But we have Eq. (A14) and that $0 \leq m_{xa} \leq 1$, so Eq. (A17) can be true only if each row consists of zeros and only one 1. Since none of p_a is zero, Eq. (A15) implies that there must be at least one 1 on each column of m. Let us arrange the x so that the first d rows of m look like an identity matrix. Then we get

$$\lambda_x = p_x \quad \text{for } x = 0, \ldots, d-1. \tag{A18}$$

Since $\sum_x \lambda_x = 1$, we have that $\lambda_x = 0$ for all $x \geq d+1$. Which is impossible because of Eq. (A13) and the fact that there must be at least one 1 on each row.

With the same argument, also $d > L$ is not possible. So, $d = L$ and Eq. (A18) holds. Also, since now $m = I$, $|S_x\rangle = |x\rangle$, rendering

$$\rho_{\text{sep}} = \sum_{a=0}^{d-1} p_a |a \ldots a\rangle\langle a \ldots a|. \tag{A19}$$

Moreover, since ρ_{sep} is unique,

$$\partial \mathcal{ENT}(S(\tau_\beta)) \cap \mathcal{SEP} \cap \mathcal{LTH} = \{\rho_{\text{sep}}\}, \tag{A20}$$

where ∂ denotes the boundary of the set.

3. Convexity of ergotropy

In this section, we take another step towards finding the maximum of the enrgotropy $W_{\max}(\rho)$ [Eqs. (3) and (A1)] over $\mathcal{SEP} \cap \mathcal{LTH}$. To that end, we prove a general result that does not depend on the particular structure of the system we discuss in this article: on the set of states with equal energy, ergotropy is a convex function.

So, say we are given the Hamiltonian $H = \sum_\alpha \mathcal{E}_\alpha |\alpha\rangle\langle\alpha|$ with $\mathcal{E}_{\alpha+1} \geq \mathcal{E}_\alpha$, $\alpha = 0, 1, \ldots$. Now, for any ρ_1 and ρ_2 such that $\mathrm{Tr}(H\rho_1) = \mathrm{Tr}(H\rho_2)$ and $\forall\ t \in [0,1]$,

$$W_{\max}[t\rho_1 + (1-t)\rho_2] \leq tW_{\max}(\rho_1) + (1-t)W_{\max}(\rho_2). \tag{A21}$$

To prove this, observe that Eq. (A21) is equivalent to

$$\mathrm{Tr}\{H[t\rho_1 + (1-t)\rho_2]^{\mathrm{passive}}\} \geq \tag{A22}$$

$$t\mathrm{Tr}(H\rho_1^{\mathrm{passive}}) + (1-t)\mathrm{Tr}(H\rho_2^{\mathrm{passive}}) = \tag{A23}$$

$$\mathrm{Tr}\{H[t\rho_1^{\mathrm{passive}} + (1-t)\rho_2^{\mathrm{passive}}]\}. \tag{A24}$$

On the other hand, as is shown in Ref. [37], for two diagonal states ρ and σ,

$$\rho \prec \sigma \Rightarrow \mathrm{Tr}(H\rho) \geq \mathrm{Tr}(H\sigma), \tag{A25}$$

where $\rho \prec \sigma$ is read as ρ is majorized by σ and means that

$$\sum_{\alpha=0}^{A} \rho_{\alpha\alpha} \leq \sum_{\alpha=0}^{A} \sigma_{\alpha\alpha}, \quad \text{for all } A = 0, 1, \ldots. \tag{A26}$$

Now, as a direct consequence of Theorem G.1. of Chap. 9 of Ref. [61], we have

$$[t\rho_1 + (1-t)\rho_2]^{\mathrm{passive}} \prec t\rho_1^{\mathrm{passive}} + (1-t)\rho_2^{\mathrm{passive}}, \tag{A27}$$

which, in view of Eq. (A25), leads to Eqs. (A22) and (A24), which prove Eq. (A21)—the main result of this section.

4. Maximization of work over $\mathcal{SEP} \cap \mathcal{LTH}$

We are now ready to prove the main claim of this section, namely,

$$\max_{\rho \in \mathcal{SEP} \cap \mathcal{LTH}} W_{\max}(\rho) = W_{\max}(\rho_{\mathrm{sep}}), \tag{A28}$$

where ρ_{sep} is from Eq. (A19).

Consider the set

$$\Sigma(S) = \mathcal{ENT}(S) \cap \mathcal{SEP} \cap \mathcal{LTH}. \tag{A29}$$

As a union of closed convex sets, Σ is a closed convex set. Equation (A21) implies that $\Sigma(S(\tau_\beta)) = \mathcal{SEP} \cap \mathcal{LTH}$. Also, obviously, when $S(\rho) > nS(\tau_\beta)$, ρ cannot be in $\mathcal{LTH}$ and, therefore, $\Sigma(S) = \emptyset$ for all $S > nS(\tau_\beta)$, and $\Sigma(nS(\tau_\beta)) = \{\tau_\beta^{\otimes n}\}$.

A convex function has its maximum over a closed convex set on the boundary (more precisely, on one of the extremal points) of that set [62]. Now, since all ρ's in $\mathcal{SEP} \cap \mathcal{LTH}$ are by definition locally thermal, they all have the same energy, $\mathrm{Tr}(H\rho) = nE_\beta$, which, according to the previous section, ensures that $W_{\max}(\rho)$ is a convex function on the whole set $\mathcal{LTH}$. Moreover, it has its maximum, $\mathcal{W}(S)$, over $\Sigma(S)$ on $\partial\Sigma(S)$. Also, since this maximum changes with S, the point delivering it lies on the boundary of $\mathcal{ENT}(S)$. On the other hand, since $\Sigma(S_1) \subset \Sigma(S_2)$ when $S_1 > S_2$, then $\mathcal{W}(S_1) < \mathcal{W}(S_2)$. Finally, as $\mathcal{W}(S)$ is a monotonically decreasing function of the global entropy, it has its maximal value at $S = S(\tau_\beta)$—the minimal possible entropy. Furthermore, because $\Sigma(S(\tau_\beta)) = \mathcal{SEP} \cap \mathcal{LTH}$,

$$\mathcal{W}(S(\tau_\beta)) = \max_{\rho \in \mathcal{SEP} \cap \mathcal{LTH}} W_{\max}(\rho), \tag{A30}$$

and this maximum is attained on the boundary of $\mathcal{ENT}(S(\tau_\beta))$. Since the latter intersects $\mathcal{SEP} \cap \mathcal{LTH}$ at only one point, ρ_{sep} [see Eq. (A20)], this means that the latter is the point where $W_{\max}(\rho)$ attains its maximal value, which proves Eq. (A28).

APPENDIX B: PROTOCOL FOR MAXIMAL WORK EXTRACTION GIVEN AN ENTROPY CONSTRAINT

In this appendix, we show that the unitary $U_{\boldsymbol{\alpha}}$, with $\boldsymbol{\alpha} = \alpha\ldots\alpha$, given by

$$\begin{aligned} U_{\boldsymbol{\alpha}}|\mathbf{i}\rangle &= \cos\alpha|\mathbf{i}\rangle + \sin\alpha|\bar{\mathbf{i}}\rangle, & \langle\mathbf{i}|H_0|\mathbf{i}\rangle &< \frac{n}{2}, \\ U_{\boldsymbol{\alpha}}|\bar{\mathbf{i}}\rangle &= -\sin\alpha|\mathbf{i}\rangle + \cos\alpha|\bar{\mathbf{i}}\rangle, & \langle\mathbf{i}|H_0|\mathbf{i}\rangle &< \frac{n}{2}, \\ U_{\boldsymbol{\alpha}}|\mathbf{i}\rangle &= |\mathbf{i}\rangle, & \langle\mathbf{i}|H_0|\mathbf{i}\rangle &= \frac{n}{2}, \end{aligned} \tag{B1}$$

produces a state $\rho = U_{\boldsymbol{\alpha}}\tau_{\beta'}(H_S)^{\otimes n}U_{\boldsymbol{\alpha}}^\dagger$ that is locally thermal with local bias z and temperature β given by

$$z = \cos(2\alpha)z', \qquad \beta = \frac{2}{E}\tanh^{-1}[\cos(2\alpha)z'], \tag{B2}$$

where $z' = \langle 0|\tau_{\beta'}|0\rangle - \langle 1|\tau_{\beta'}|1\rangle = \mathrm{Tr}(\sigma_z\tau_{\beta'})$ is the bias of $\tau_{\beta'}$ [where, for the sake of brevity, we now write $\tau_{\beta'}$ in place of $\tau_{\beta'}(H_S)$ since no confusion should arise]. To see that this is the case, we note first that ρ is symmetric under permutations, since both the initial state $\tau_{\beta'}(H_S)^{\otimes n}$ and U_α are symmetric. Therefore, it suffices to calculate $z_1 = \langle 0|\rho_1|0\rangle - \langle 1|\rho_1|1\rangle$. We note first that this can be rewritten as follows:

$$z_1 = \mathrm{Tr}(\sigma_z \rho_1) = \mathrm{Tr}(\sigma_z \otimes \mathbb{1}_{n-1}\rho) = \sum_{i_1 \ldots i_n} \langle \mathbf{i}|(-1)^{i_1}\rho|\mathbf{i}\rangle. \tag{B3}$$

Now, it is straightforward to see that

$$\langle \mathbf{i}|\rho|\mathbf{i}\rangle = \langle \mathbf{i}|U_\alpha \tau_{\beta'}^{\otimes n} U_\alpha^\dagger|\mathbf{i}\rangle = \cos^2\alpha \langle \mathbf{i}|\tau_{\beta'}^{\otimes n}|\mathbf{i}\rangle + \sin^2\alpha \langle \bar{\mathbf{i}}|\tau_{\beta'}^{\otimes n}|\bar{\mathbf{i}}\rangle \tag{B4}$$

holds for all $|\mathbf{i}\rangle$, and furthermore that $\langle \mathbf{i}|\tau_{\beta'}|\mathbf{i}\rangle = \frac{1}{2}[1 + (-1)^i z']$, which follows from the definition of z' as the bias. Put together, this allows one to reexpress z_1 as

$$z_1 = \sum_{i_1,\ldots,i_n} (-1)^{i_1} \left(\frac{\cos^2\alpha}{2^n} \prod_k [1 + (-1)^{i_k} z'] + \frac{\sin^2\alpha}{2^n} \prod_k [1 + (-1)^{i_k}(-z')] \right), \tag{B5}$$

which, upon interchanging the order of the product and sum, becomes

$$z_1 = \frac{\cos^2\alpha}{2^n} \prod_{i_1,\ldots,i_n} \sum_{i_k} (-1)^{i_1}[1 + (-1)^{i_k} z'] + \frac{\sin^2\alpha}{2^n} \prod_{i_1 \ldots i_n} \sum_{i_k} (-1)^{i_1}[1 + (-1)^{i_k}(-z')]. \tag{B6}$$

For $k \neq 1$, $\sum_{i_k}(-1)^{i_1}[1 + (-1)^{i_k} z'] = 2$, while for $k = 1$, $\sum_{i_k}(-1)^{i_1}[1 + (-1)^{i_k} z'] = 2z'$, from which we finally obtain

$$z_1 = \cos^2(\alpha) z' + \sin^2(\alpha)(-z') = \cos(2\alpha) z'. \tag{B7}$$

1. Presence of entanglement in the state

Consider the state $\rho = U_{\boldsymbol{\alpha}} \boldsymbol{\tau}_{\beta'}^{\otimes n} U_{\boldsymbol{\alpha}}^\dagger$. As it has an X-like shape, applying the criterion of positivity under partial transposition (PPT) [63,64] with respect to a bipartition $A|\bar{A}$ to ρ will yield an independent positivity condition for each pair of coherences $\langle \mathbf{i}|\rho|\bar{\mathbf{i}}\rangle$, $\langle \bar{\mathbf{i}}|\rho|\mathbf{i}\rangle$, given by

$$|\langle \mathbf{i}|\rho|\bar{\mathbf{i}}\rangle| - \sqrt{\langle \mathbf{i}|\langle \bar{\mathbf{i}}|\Pi_{A|\bar{A}} \rho^{\otimes 2} \Pi_{A|\bar{A}}|\mathbf{i}\rangle|\bar{\mathbf{i}}\rangle} \geq 0, \tag{B8}$$

where $\Pi_{A|\bar{A}}$ is the permutation operator acting on the two-copy Hilbert space exchanging partition A between the two copies. Focusing on $|\mathbf{i}\rangle = |0\ldots0\rangle$, $|\bar{\mathbf{i}}\rangle = |1\ldots1\rangle$ and on the bipartition $(n/2|n/2)$, the condition for nonseparability reads:

$$\sin(2\alpha)(1 - e^{-\beta' \epsilon n}) - 2e^{-\beta' \epsilon n/2} \geq 0. \tag{B9}$$

For sufficiently large n, entanglement will be present in the state for any α. Indeed, when $S(\rho) \propto n$, β' is a constant, and so is α. So, for n large enough, the lhs of Eq. (B9) will be $\approx \sin(2\alpha)$, which is ≥ 0. In all other cases, i.e., when $S(\rho) \not\propto n$, which means $S(\tau_{\beta'}) = (S(\rho)/n) \to 0$ (with $n \to \infty$), $e^{-\beta'\epsilon}$ decreases, so $z' = (1 - e^{-\beta'\epsilon}/1 + e^{-\beta'\epsilon})$ increases, so $\cos(2\alpha) = (z/z')$ decreases, so $\sin(2\alpha)$ increases. All in all, the lhs of Eq. (B9) increases with n, becoming positive starting from some value of n.

2. Maximal work extraction from states with submacroscopic entropy

Here, we show that when the entropy of the global state $S(\rho)$ is submacroscopic, i.e.,

$$x_n = \frac{S(\rho)}{n} \to 0, \quad \text{when } n \to \infty, \tag{B10}$$

the maximal work extractable from locally thermal separable states, $W_{\mathrm{sep}}[S(\rho)]$, and from general entangled locally thermal states, $W_{\max}[S(\rho)]$ [Eq. (11)], asymptotically coincide:

$$\lim_{n\to\infty} \frac{W_{\mathrm{sep}}[S(\rho)]}{W_{\max}[S(\rho)]} = 1. \tag{B11}$$

First, we observe that, trivially,

$$\frac{W_{\mathrm{sep}}[S(\rho)]}{W_{\max}[S(\rho)]} \leq 1. \tag{B12}$$

We then start by asymptotically expanding $W_{\max}[S(\rho)]$. For that we need the asymptotics of $E_{\beta'}$ when $S(\tau_{\beta'}) = x_n$. Denote $p' = e^{-\beta' E}/\mathcal{Z}'$. Then, $E_{\beta'} = p' E$. Now, since $x_n \to 0$, p' also has to $\to 0$. Therefore,

$$x_n = -p' \ln p' - (1 - p') \ln(1 - p') = p' \ln \frac{1}{p'} + \mathcal{O}(p').$$

Hence,

$$p' = \frac{x_n}{\ln \frac{1}{x_n}} \left[1 + \mathcal{O}\left(\frac{\ln \ln \frac{1}{x_n}}{\ln \frac{1}{x_n}} \right) \right]. \tag{B13}$$

And since the final energy is simply $nE_{\beta'} = np'E$, we have

$$W_{\max} = nE_\beta - \frac{S}{\ln n - \ln S}[1 + o(1)] \sim nE_\beta. \tag{B14}$$

Let us now consider the following three-parameter family of diagonal states:

$$\Omega(\epsilon,\delta,\gamma)=\epsilon|0\rangle\langle 0|^{\otimes n}+\delta|1\rangle\langle 1|^{\otimes n}+\frac{\gamma}{C_n^D}\sum_{|\mathbf{i}|=D}|\mathbf{i}\rangle\langle\mathbf{i}|, \quad \text{(B15)}$$

where D is the smallest number satisfying $\ln C_n^D \geq S$, and ϵ, δ, and γ are non-negative and, from the normalization condition,

$$\epsilon+\delta+\gamma=1. \quad \text{(B16)}$$

Furthermore, the local thermality requires

$$\delta+\gamma\frac{D}{n}=\frac{e^{-\beta E}}{\mathcal{Z}}\equiv p. \quad \text{(B17)}$$

And finally, the entropy must be S:

$$-\epsilon\ln\epsilon-\delta\ln\delta-\gamma\ln\gamma+\gamma\ln C_n^D=S. \quad \text{(B18)}$$

Resolving Eqs. (B16) and (B16), we reformulate Eq. (B18) as

$$f(\gamma)=S, \quad \text{(B19)}$$

where

$$f(\gamma)=-\left(1-p-\gamma\frac{n-D}{n}\right)\ln\left(1-p-\gamma\frac{n-D}{n}\right)-\left(p-\gamma\frac{D}{n}\right)\ln\left(p-\gamma\frac{D}{n}\right)-\gamma\ln\gamma+\gamma\ln C_n^D.$$

Now, $f(\gamma)$ is a continuous function on [0,1], and $f(0)=-p\ln p-(1-p)\ln(1-p)=S(\tau_\beta)\leq S$ and $f(1)=\ln C_n^D$, which, by the very definition of D, exceeds S. So, $S\in[f(0),f(1)]$ and, due to the continuity of $f(\gamma)$, $\exists\,\gamma$ such that Eq. (B19) is satisfied. We denote that value of γ via γ_0, and the state Ω it (uniquely) determines via Ω_0.

Finally, we note that since the rank of Ω_0 is at most $2+C_n^D$, the passive state associated with it will occupy the first $2+C_n^D<C_n^{D+1}$ energy levels. Therefore, the energy of Ω_0 is $<(D+1)E$. Hence,

$$W_{\text{sep}}>nE_\beta-(D+1)E. \quad \text{(B20)}$$

On the other hand, $D<S$. Indeed, due to the general inequality $C_n^k\geq(n/k)^k$, we have $\ln C_n^S\geq S\ln\frac{n}{S}$. Since $S/n\to 0$, for sufficiently big n, we will have $n/S>e$, which leads to $\ln C_n^S>S$, implying that $D<S$. Thereby, we end up with

$$W_{\text{sep}}>nE_\beta-SE, \quad \text{(B21)}$$

which, taking into account Eq. (B14), leaves us with

$$\frac{1-\frac{S}{n}\frac{E}{E_\beta}}{1-\frac{S}{n}\frac{1+o(1)}{\ln n-\ln S}}<\frac{W_{\text{sep}}(S(\rho))}{W_{\max}(S(\rho))}\leq 1. \quad \text{(B22)}$$

In view of $S/n\to 0$, Eq. (B22) finalizes the proof of Eq. (B11).

3. Maximal work extraction from states with macroscopic entropy

In what follows, we show that in the asymptotic limit it is possible to approximately achieve maximal work extraction given an entropy constraint from a state that is classical. To do so, we apply the unitary $U_{\boldsymbol{\alpha}}$ with $\boldsymbol{\alpha}$ chosen appropriately. Consider that α_k is nonzero (and equal to $\pi/2$) only for $k=np'-\mu\equiv\ell$, i.e., between the subspaces with $|\mathbf{i}|=np'-\mu$ and $|\bar{\mathbf{i}}|=n(1-p')+\mu$, where $p'=\langle 1|\tau_{\beta'}|1\rangle=\frac{1}{2}(1-z')$ is the excited state probability in $\tau_{\beta'}$. That is, we consider the unitary V:

$$V|\mathbf{i}\rangle=|\bar{\mathbf{i}}\rangle,\qquad V|\bar{\mathbf{i}}\rangle=-|\mathbf{i}\rangle\quad\text{if }|\mathbf{i}|=np'-\mu$$
$$V|\mathbf{i}\rangle=|\mathbf{i}\rangle\quad\text{if }|\mathbf{i}|\neq np'-\mu.$$

Obviously, after applying V the state is still diagonal and symmetric. This means that the transformed state is again locally thermal, but now with the new bias $z''=1-2p''$. To find it, we observe that the energy of the global state is given by nEp''. On the other hand, V swapped the population of the level ℓE, $C_n^\ell(p')^\ell(1-p')^{n-\ell}$, with $C_n^{n-\ell}(p')^{n-\ell}(1-p')^\ell$, the population of $(n-\ell)E$. As a result, the initial energy $np'E$ increased by $C_n^\ell[(p')^\ell(1-p')^{n-\ell}-(p')^{n-\ell}(1-p')^\ell](n-2\ell)E$. This implies, that

$$p''=p'+C_n^\ell[(p')^\ell(1-p')^{n-\ell}-(p')^{n-\ell}(1-p')^\ell]\times(1-2\ell/n),$$

or, equivalently,

$$z''=z'-2C_n^\ell(z'+2\mu/n)[(p')^\ell(1-p')^{n-\ell}-(p')^{n-\ell}(1-p')^\ell]. \quad \text{(B23)}$$

Now, let us focus on $\mu\leq\mathcal{O}(\sqrt{n})$ (we show that this set is enough for our purposes). We then have the asymptotic expansion

$$(p')^{np'-\mu}(1-p')^{n(1-p')+\mu}C_n^{np'-\mu}=\frac{e^{-[\mu^2/2p'(1-p')n]+\mathcal{O}(\mu/n)}}{\sqrt{2\pi np'(1-p')}}, \quad \text{(B24)}$$

using which it is straightforward to obtain from Eq. (B23) that

$$z'' = z' - z' \frac{e^{-[\mu^2/2p'(1-p')n]+\mathcal{O}(\mu/n)}}{\sqrt{2\pi n p'(1-p')}}(1 - e^{-\beta'(nz'+2\mu)E}).$$

Clearly, for $\mu \leq \mathcal{O}(\sqrt{n})$,

$$z'' = z' - \mathcal{O}(1/\sqrt{n}). \tag{B25}$$

On the other hand, observe that the left-hand side of Eq. (B24) is the population of the level $np' - \mu$, and the summation of these values over all $\mu \leq \mathcal{O}(\sqrt{n})$ will produce $1 - \mathcal{O}(1/\sqrt{n})$. Hence, if we apply the inversions described by V on all levels with $\mu \leq \mathcal{O}(\sqrt{n})$, we will arrive at a state with local bias being $-z' + \mathcal{O}(1/\sqrt{n})$. Now, since each inversion changes the initial bias by $\mathcal{O}(1/\sqrt{n})$ [Eq. (B25)], we conclude that by conducting a sequence $\mathcal{O}(\sqrt{n})$ steps, one can change the initial local bias z' to any $|z| < z'$, with the precision increasing with n. Therefore, in the thermodynamic limit there exist diagonal states that asymptotically saturate the thermodynamic bound Eq. (11).

APPENDIX C: CORRELATIONS IN DEGENERATE SUBSPACES

Consider the total Hamiltonian

$$H = \sum_{i=1}^{n} h_i = \sum_{i=1}^{n_l} E_i \Pi_i, \tag{C1}$$

where each $h_i = h := \sum_{a=0}^{d-1} \epsilon_a |a\rangle\langle a|$ (with $\epsilon_0 = 0$) has local dimension d, which we assume to be finite. The number of different global energies n_l is found to be

$$n_l = C_{n+d-1}^{d-1} = \frac{(n+d-1)!}{n!(d-1)!}, \tag{C2}$$

which corresponds to the number of nonzero eigenvalues of Eq. (12). In order to find the passive state associated with Eq. (12), one has to move such eigenvalues to the lowest energy levels. This operation requires knowledge of the spectrum of h_i. Nevertheless, it suffices for our purposes to move them to a sufficiently degenerate energy. The degeneracy of a global energy $E_i = \sum_j k_j^{(i)} \epsilon_j$ is equal to $C_n^{k_1^{(i)}, k_2^{(i)}, \ldots, k_d^{(i)}}$. The point is then to find the lowest energy, $E_{\min}$, satisfying $C_n^{k_1^{\min}, k_2^{\min}, \ldots, k_d^{\min}} \geq C_{n+d-1}^{d-1}$, so that the work extracted after such a transformation is simply given by

$$W_{\deg} \geq E_{\rho_{\deg}} - E_{\min}. \tag{C3}$$

Now, notice that for large n,

$$\lim_{n\to\infty} \frac{C_{n+d-1}^{d-1}}{C_n^{n-d, k_2', \ldots, k_d'}} = 0, \qquad \sum_{j=2}^{d} k_j' = d, \tag{C4}$$

with $E' = \sum_{a=2}^{d} k_a' \epsilon_a$. Observe that E' is of the order of the energy of one subsystem (for instance, choosing $k_2' = d$ and $k_j' = 0$ for $j > 2$, we obtain $E' = d\epsilon_2$). Therefore, we can take $E_{\min} = E'$, obtaining the desired result.

In the case of $d = 2$, the expression for $E_{\min}$ is particularly simple:

$$W_{\min} = [1 - C_n^{pn} p^{np} (1-p)^{(1-p)n}]E. \tag{C5}$$

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