What is the temperature of a quantum state?

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Temperature is usually defined for physical systems at thermal equilibrium. Nevertheless one may wonder if it would be possible to attribute a meaningful notion of temperature to an arbitrary quantum state, beyond simply the thermal (Gibbs) state. In this work, we propose such a notion of temperature considering an operational task, inspired by the Zeroth Law of thermodynamics. Specifically, we define two effective temperatures for quantifying the ability of a quantum system to cool down or heat up a thermal environment. In this way we can associate an operationally meaningful notion of temperature to any quantum density matrix. We provide general expressions for these effective temperatures, for both single- and many-copy systems, establishing connections to concepts previously discussed in the literature. Finally, we consider a more sophisticated scenario where the heat exchange between the system and the thermal environment is assisted by a quantum reference frame. This leads to an effect of “coherent quantum catalysis”, where the use of a coherent catalyst allows for exploiting quantum energetic coherences in the system, now leading to much colder or hotter effective temperatures.

I. INTRODUCTION

Temperature is a well-defined property of macroscopic systems in thermal equilibrium [1]. When considering equilibrium systems of finite size, subtleties on the notion of temperature can arise due to the breakdown of the equivalence of statistical ensembles [2–8] and the non-negligible effect of interactions between constituents [9–13]. Moving on to non-equilibrium (quantum) systems, assigning an effective temperature can be useful in certain physical contexts [14–17].

Given some quantum state $\rho$ evolving under Hamiltonian $H$, the most common approach is to assign an effective temperature $T^*$ given by the temperature of an equilibrium (Gibbs) state with the same average energy, that is

$$\text{Tr}[H\rho] = \text{Tr}[H\gamma(T^*, H)]$$

where $\gamma(T, H) \equiv e^{-\beta H}/Z$, $Z = \text{Tr} e^{-\beta H}$ is the partition function and $\beta = 1/k_B T$ ($k_B = 1$ in what follows). The relevance of the identification (1) naturally arises in the dynamics of isolated quantum many-body systems: seminal results suggest that $\rho$ will become indistinguishable from $\gamma(T^*, H)$ after a transient thermalisation time [18][19–24]. Beyond many-body isolated systems, different notions of effective temperatures have been discussed for characterizing non-equilibrium steady states, including those appearing in autonomous thermal machines [25–28] and engines powered by squeezed reservoirs [29–31].

Here we propose an alternative approach for defining temperature for an arbitrary quantum system. Our approach is operational and inspired by the Zeroth Law of thermodynamics. We consider a system with Hamiltonian $H$ in a quantum state $\rho$, and place it in contact with another (reference) system initially at thermal equilibrium. We then assign two temperatures for the system, $T_c$ and $T_h$, which correspond to the lowest and the highest (real) temperatures at which the reference system can be cooled down or heated up. That is, $T_c$ and $T_h$ characterize the potential of $\rho$ to heat up or cool down a reference state in thermal equilibrium (see Fig. 1). A direct consequence of this approach is to establish a natural direction of heat flow between $\rho$ and a thermal environment at temperature $T$: Heat will always flow towards the environment when $T \leq T_c$ and, likewise, the environment will always absorb heat when $T \geq T_h$. Instead, for $T_c \leq T \leq T_h$, the direction of heat flow depends on the particular process. As expected, $T_c \leq T^* \leq T_h$, with equality when the system itself is in thermal equilibrium with temperature $T^*$.

We apply this approach to three different situations. First, we find that the effective temperatures of microscopic quantum systems are directly related with virtual temperatures [25–28]. Second, we show that for macroscopic quantum systems, the two effective temperatures are closely related to the effective temperature $T^*$. Third, we extend the framework by introducing a reference frame, or a quantum catalyst [32–38]. This gives access to strictly colder and hotter effective temperatures by exploiting energy coherences present in the system. In other words, the catalyst enables a genuinely quantum mechanism for transferring heat by converting coherences into energy. To the best of our knowledge, this provides a new interpretation of energy superposition in quantum thermodynamics as a resource for generating flows of heat, and emphasizes the role of genuinely quantum catalytic effects in thermodynamics.

II. OPERATIONAL DEFINITION OF TEMPERATURE

In what follows a physical system $S$ will be described by a tuple $(H_S, \rho_S)$, where $H_S$ stands for the system Hamiltonian and $\rho_S$ its density matrix. We will say that a system is in thermal equilibrium with respect to the real temperature $T$ if its state can be written as $\rho_S = \gamma(S, T, H_S)$.

The Zeroth Law of thermodynamics postulates that there is a form of energy called heat, and a scalar quantity, called temperature, that measures its propagation between physical systems [39, 40]. When system $A$ is in a thermal equilibrium with another system $B$ that is in a thermal equilibrium with $C$, then $A$ must be in a thermal equilibrium with $C$. This validates the use of suitable thermodynamic systems as thermometers: If $C$ has a well-defined temperature $T$, then $B$ can be used to determine the temperature of $A$ (see Fig. 1a). Importantly, the Zeroth Law associates temperature with systems.
In thermal equilibrium. In what follows we will use a similar approach to define effective temperatures for systems out of equilibrium. We will consider three thermodynamic systems: $A$, $B$ and $C$, where $C$ is a macroscopic heat bath with a real temperature $T$, system $B \equiv (H_B, \gamma(T, H_B))$ is a thermometer probe, and $A \equiv (H_A, \rho_A)$ is the quantum system whose effective temperatures we want to infer. For that, we consider the following steps: (i) we couple $B$ to $C$ until $B$ reaches thermal equilibrium at temperature $T$, (ii) we couple them, and (iii) we couple $B$ to $A$ to infer the effective temperature of $A$ by measuring $B$.

Let us now describe in detail step (iii), where the thermometer $B$ and $A$ interact. First, we demand that energy is preserved within the joint system $AB$. More precisely, we assume that $A$ interacts with $B$ via some interaction Hamiltonian $H_{\text{int}}(t)$ for some time $t$, so that they evolve together according to a unitary

$$U(t) = \exp \left( -\frac{i}{\hbar} \int_0^t [H_A + H_B + H_{\text{int}}(s)] \, ds \right)$$

that preserves the total energy of the composite system, i.e. $[H_{\text{int}}(t), H_A + H_B] = 0$, or equivalently, $[U(t), H_A + H_B] = 0$ at all times $t$. In other words, although an external field may be applied to generate the interaction, the total work done by the field is at all times zero. This ensures that only the free energy of $A$ is used to heat up or cool down the thermometer. Second, we assume perfect control over the joint system, meaning we allow for arbitrary interactions $H_{\text{int}}(t)$ and arbitrary long times $t$. The dynamics is then fully characterized by the set of energy-preserving unitaries [41, 42]. To simplify notation from now we omit the time dependence and write $U$ instead of $U(t)$. Notice that we make no assumptions about the strength of interaction (weak or strong), its complexity (local or collective), nor duration (short or long) with respect to the natural time scales of the systems involved. Third, we assume the initial state of $AB$ factorizes, i.e. $\rho_{AB} = \rho_A \otimes \gamma_B (T, H_B)$. This ensures that $B$ has a well-defined temperature and its energy changes may be interpreted as heat.

The joint state of the system and the thermometer after the interaction is given by $\sigma_{AB} = U [\rho_A \otimes \gamma_B(\beta, H_B)] U^\dagger$. The heat transferred to the thermometer is therefore

$$Q(T, H_B, U) := \text{Tr} \left[ H_B (\sigma_B - \gamma_B(T, H_B)) \right]$$

with $\sigma_B := \text{Tr}_A \sigma_{AB}$. It is well-known that heat can only flow in one direction when $A$ is a Gibbs state at some temperature $T(A)$, i.e. $\rho_A = \gamma_A(T(A), H_A)$. More specifically,

$$Q(T, H_B, U) \geq 0 \quad \text{for all} \quad T \leq T(A),$$

$$Q(T, H_B, U) \leq 0 \quad \text{for all} \quad T \geq T(A),$$

which holds for all possible $H_B$ and $U$ [43, 44]. In other words, the direction of heat is well-defined between Gibbs states: Heat can only flow from hot to cold, regardless of the particular thermometer $B$ or process $U$. Instead, for non-thermal states the direction of heat flow is not always unique, as illustrated by its reversal in the presence of correlations [43–46]. That is, the sign of $Q(T, H_B, U)$ in general depends on $H_B$ and the process $U$.

The crucial insight of our work is that there are temperatures for which heat has a well-defined direction even for non-equilibrium states (i.e., it is independent of $H_B$ and $U$ and depends only on $A$). Given some $A = (H_A, \rho_A)$, we will show that there exist temperatures $T_c(A)$ and $T_h(A)$ that satisfy

$$Q(T, H_B, U) \geq 0 \quad \text{for all} \quad T \leq T_c(A),$$

$$Q(T, H_B, U) \leq 0 \quad \text{for all} \quad T \geq T_h(A),$$

for all possible $H_B$ and $U$, in complete analogy with the equilibrium case (4). That is, we can say, without ambiguities, than $A$ is hotter/colder than any equilibrium state below/above the temperatures $T_c(A)$ and $T_h(A)$, respectively. Conversely, $A$ has the potential to cool down an equilibrium reference state with temperature $T \geq T_c$ (and similarly to heat up states with $T \leq T_h$). Hence, $T_c$ and $T_h$ give bounds on the ability of $A$ to heat up or cool down a thermal environment. As expected, for Gibbs states $T(A) = T_c(A) = T_h(A)$, whereas for non-equilibrium systems $T_c(A) \neq T_h(A)$.

In order to find the effective cold $T_c(A)$ and hot $T_h(A)$ temperatures, we look for the minimal (maximal) reference temperature $T$ for which $Q(B)$ is negative (positive) for some thermometer $B$ and some energy-preserving interaction $U$, i.e.
\[ T_c(A) := \min_{H_B, U} T \]
\[ \text{s.t. } Q(T, H_B, U) < 0, \quad [U, H_A + H_B] = 0. \]

In a similar manner we define \( T_h(A) \) by replacing \( \min \) with \( \max \) above and reversing the inequality.

### A. Effective temperatures of single-copy quantum systems

The effective channel acting on the system \( A \) is of the form

\[ \mathcal{E}_T(\cdot) = \text{Tr}_B[U(\cdot \otimes \gamma_B(T, H_B))U^\dagger]. \]

This is a well-studied class of quantum channels known as thermal operations [33, 41, 47, 48]. This correspondence can be used to express the problems defining our effective temperatures from \( A \), which are known as virtual temperatures [25]. Following [41, 50, 51], we define the virtual temperature as an average over the orbit, i.e. a state dephased in the energy basis, and ultimately renders energy superpositions irrelevant from the perspective of cooling or heating the thermometer.

In what follows we discuss two ways to overcome this restriction. First, we consider processing multiple copies of the system collectively and show that the degeneracy of energy levels allows to exploit coherence locked in the quantum system. Second, we extend the framework by introducing a reference frame, i.e. a system that allows to locally lift some of the restrictions imposed by the presence of conserved quantities.

### B. Effective temperatures of macroscopic quantum systems

Suppose that system \( A \) consists of multiple identical copies, i.e. \( A \equiv A^n := (H_A^\otimes n, \rho_A^\otimes n) \), with \( n \) large (see Fig. 1c). It is well known that energy of any \( n \)-copy state, for sufficiently large \( n \), can be unitarily increased as long as the state is out of equilibrium [52]. As we will see, this is also true in the presence of an energy-conservation law. Therefore, for asymptotically large systems it is more natural to assign effective temperatures only when a certain amount of heat can be delivered or accepted by the composite system. In what follows a large system \( A^n \) composed of \( n \) particles will be considered hotter than \( T \) if there is a thermometer \( B \) and an interaction \( U \) such that the thermometer is heated up by a certain amount, and similarly for the case of cooling. This motivates extending the definition of effective temperatures by introducing a parameter \( \delta > 0 \) that captures the minimal amount of heat that must be transferred to (or accepted by) the thermometer, i.e.

\[ T_c(A, \delta) := \min_{H_B, U} T \]
\[ \text{s.t. } Q(T, H_B, U) \leq -\delta, \quad [U, H_A + H_B] = 0. \]

We obtain the definition for \( T_h(A) \) by replacing \( \min \) with \( \max \) with \( \delta \) and reversing the side of the inequality and changing \( \delta \rightarrow -\delta \). For consistency, we can immediately verify that \( \lim_{\delta \rightarrow 0^+} T_c(A, \delta) = T_c(A) \). Intuitively, while \( T_c(A) \) and \( T_h(A) \) correspond to the minimal and maximal virtual temperatures of \( A \), the temperatures \( T_c(A, \delta) \) and \( T_h(A, \delta) \) depend on the whole spectrum of virtual temperatures.

In Appendix A we show that for any quantum system \( A \)

In Appendix A we show that for any quantum system \( A \) with \( H_A = \sum \epsilon_i | \epsilon_i \rangle \langle \epsilon_i | \) and \( p_i := \langle \epsilon_i \rho_A | \epsilon_i \rangle \), the effective temperatures are given by

\[ T_c(A) = \min_{i \neq j} T_{ij}, \quad T_h(A) = \max_{i \neq j} T_{ij}, \]

where \( T_{ij} := (\epsilon_i - \epsilon_j)/\log(p_i/p_j) \). The proofs proceed similarly for both effective temperatures, so let us focus on \( T_c(A) \). First, we show that for any quantum system \( A \) there is always a simple interaction and a qubit thermometer that can be cooled down when \( T \geq \min_{i \neq j} T_{ij} \). Then we use a resource-theoretic formulation of the problem to show that there is no thermometer system \( B \) that can be cooled down using \( A \) when \( T \leq \min_{i \neq j} T_{ij} \). This proves that \( T_c(A) \) is equal to \( \min_{i \neq j} T_{ij} \). For full details see Appendix A.

The above result is related to the concept of virtual (or effective) temperatures that characterize the behavior of quantum thermal machines operating between two baths at different temperatures [25–28, 49]. When looking at the baths together, a special two-dimensional subspace in the Hilbert space of the composite bath can be distinguished (so-called virtual qubit). In the weak-coupling limit this subspace behaves effectively as an equilibrium system at a certain virtual temperature different from the temperature of the respective baths. An external system interacting with these baths reacts as if put in contact with a real qubit at the given virtual temperature [25]. Following [41, 50, 51], one can define virtual temperatures for a single quantum systems by constructing a set \( \{ T_{ij} \mid 1 \leq i, j \leq d_A \text{ and } \langle i | H_A | i \rangle \neq \langle j | H_A | j \rangle \} \). Our result then states that the minimal and maximal virtual temperatures of a single quantum system \( A \) are operationally meaningful: They can be interpreted, respectively, as the lowest and highest temperature of a fictitious equilibrium state that can be cooled down or heated up when put in contact with \( A \).

A quantum system \( A \) is out of equilibrium with respect to a reference temperature \( T \) when it contains at least one virtual temperature different from \( T \). Moreover, since virtual temperatures depend only on the occupations in the energy basis, superpositions of different energy levels have exactly the same ability to generate heat as corresponding probabilistic mixtures of energy levels. This is a consequence of the time-translation symmetry of the effective dynamics on \( A \) resulting from resonant (energy-conserving) interactions. More specifically, the restriction \( [U, H_A + H_B] = 0 \) implies that every channel of the form \( (7) \) is symmetric under translations in time, that is \( e^{-iH t} \mathcal{E}_T(\rho)e^{iH t} = \mathcal{E}_T(e^{-iH t}\rho e^{iH t}) \) for all \( t \). This can be seen as a limitation caused by the lack of a clock capable of measuring time. When the system is prepared in a state \( | \psi_A \rangle \), it cannot be distinguished from any other state in the orbit of \( e^{-iH_A t} \). This ignorance obligates us to describe it as an average over the orbit, i.e. a state dephased in the energy basis, and ultimately renders energy superpositions irrelevant from the perspective of cooling or heating the thermometer.

In what follows we discuss two ways to overcome this restriction. First, we consider processing multiple copies of the system collectively and show that the degeneracy of energy levels allows to exploit coherence locked in the quantum system. Second, we extend the framework by introducing a reference frame, i.e. a system that allows to locally lift some of the restrictions imposed by the presence of conserved quantities.
fore we define the asymptotic effective temperatures as
\[ T_{c/h}^\infty(\delta) \equiv \beta_{c/h}^\infty(\delta)^{-1} := \lim_{n \to \infty} T_{c/h}(\rho_A, n\delta). \] (10)

In Appendix B we show that \( \beta_{c/h}^\infty(\delta) \) can be expressed as
\[ \beta_{c/h}^\infty(\delta) = \frac{1}{\delta} \left[ S(\gamma_A(E + \delta)) - S(\gamma_A(E + \delta)) \right], \] (11)
\[ \beta_{h}^\infty(\delta) = \frac{1}{\delta} \left[ S(\gamma_A(E - \delta)) - S(\gamma_A(E - \delta)) \right], \] (12)

where \( \gamma_A(x) \) stands for a Gibbs state with Hamiltonian \( H_A \) and average energy \( x \), parameter \( E := \text{tr}(\rho_A H_A) \) and \( S(\rho) := -\text{Tr} \ln \rho \) is the von Neuman entropy.

To develop some intuition about the effective temperatures we can look at the standard thermodynamic limit. Here it corresponds to the regime with \( n \to \infty \) and \( \delta \to 0 \) and the system \( A \) prepared in a Gibbs state with average energy \( E \), i.e. \( \rho_A = \gamma_A(E) \). In this regime \( \beta_{c/h}^\infty(\delta) \) both converge to the usual definition of temperature, i.e.
\[ \lim_{\delta \to 0} \beta_{c/h}^\infty(\delta) = \frac{\Delta S(\rho_A)}{\delta} + \beta^*(E) - \frac{\delta}{2\Delta^2 E(\gamma_A)}. \] (13)

For any quantum state \( \rho_A \) we can further expand up to \( O(\delta^2) \),
\[ \beta_{c/h}^\infty(\delta) \approx \pm \frac{\Delta S(\rho_A)}{\delta} + \beta^*(E) - \frac{\delta}{2\Delta^2 E(\gamma_A)}, \] (14)
where \( \Delta S(\rho_A) := S(\gamma_A(E)) - S(\rho_A) \) and \( \Delta^2 E(\gamma_A) := \text{tr} [H_A^2 \gamma_A(E)] - \text{tr} [H_A \gamma_A(E)]^2 \). Expression (14) naturally connects \( \beta_{c/h}^\infty(\delta) \) with the effective temperature \( \beta^* \) defined in Eq. (1). For generic states \( \beta_{c/h}^\infty(\delta) \) differ, i.e. quantum systems can be both hot and cold, even in the asymptotic limit. Note that \( \beta_{c/h}^\infty(\delta) \) diverge in the limit \( \delta \to 0 \), indicating that an asymptotically large source of non-equilibrium can cool down or heat up reference systems at any temperature by a sublinear amount in \( n \).

C. Quantum catalysis and the role of quantum coherence

Time-translation symmetry implies it is always possible to explain the resulting mechanism of transferring heat classically, i.e. using classical (stochastic) systems with the same distributions of energy. We saw this is no longer true when many copies of the system are processed collectively. Now we take a different approach where effective temperature is assigned to a single quantum system using a quantum reference frame [53–58]. This leads to a genuinely quantum behavior where energy coherence plays an active role in generating the flow of heat, even at the level of a single quantum system.

Let us begin with a motivating example. Consider a qutrit \( A = (\rho_A, H_A) \) with \( H_A = |1\rangle \langle 1| + 2|2\rangle \langle 2| \) and
\[ \rho_A = (1 - \lambda) \gamma_A(H_A, \beta) + \lambda |\psi\rangle \langle \psi|, \] (15)
where \( |\psi\rangle = (|0\rangle + |1\rangle + |2\rangle) / \sqrt{3} \) and \( 0 \leq \lambda \leq 1 \). To focus our attention, let us first consider the case \( \beta = \infty \). The energy populations then correspond to a thermal state at infinite temperature, i.e. \( \gamma_A(H_A, \infty) = \frac{1}{3}, \) and the effective temperatures coincide, \( \beta_c(A) = \beta_h(A) = 0 \). We further assume access to a qubit reference frame \( R = (\omega_R, H_R) \) with \( H_R = |1\rangle \langle 1| \) and \( \omega_R = \frac{1}{2} \left( 1 - \frac{1}{\sqrt{2}} \right) |2\rangle + \frac{1}{\sqrt{2}} |\rangle \rangle \). The joint system \( AR \) has two degenerate energy eigenspaces spanned, respectively, by \( \{|01\rangle, |10\rangle\} \) and \( \{|20\rangle, |11\rangle\} \). The protocol we consider consists of a preprocessing step in which system \( A \) interacts resonantly with \( R \) in these degenerate subspaces, and a cooling/heating step where the actual transfer of heat between \( A \) and \( B \) is carried out. For preprocessing, we consider a unitary \( V \) acting as
\[ V |01\rangle = \frac{|01\rangle - |10\rangle}{\sqrt{2}}, \quad V |10\rangle = \frac{|10\rangle + |01\rangle}{\sqrt{2}}, \] (16)
\[ V |20\rangle = \frac{|20\rangle + |11\rangle}{\sqrt{2}}, \quad V |11\rangle = \frac{|20\rangle + |11\rangle}{\sqrt{2}}. \] (17)

Clearly, \( [V, H_{AR}] = 0 \) and \( V \) rotates the initial state into \( \sigma_{AR} = V \rho_A \otimes \omega_R V^\dagger \) that leads to the reduced state
\[ \sigma_A = \frac{1}{12} \begin{pmatrix} 4 + \sqrt{2} & x_+ & 2x_+ \\ x_- & 4 - 2\sqrt{2} & x_- \\ 2x_+ & x_- & 4 + \sqrt{2} \end{pmatrix}, \] (18)
with \( x_\pm = (\sqrt{2} \pm 1)/2 \). Since the marginal state of the catalyst remains the same, \( \sigma_R = \omega_R \), the process can be viewed as a correlated-catalytic transformation [59]. Notice that the state of \( A \) is now different from the Gibbs state at infinite
temperature: We redistributed its energy population using its internal coherence. A simple calculation reveals that the effective temperatures of \( \sigma_A \), denoted \( \beta_{c/h}(A|R) \), are given by

\[
\beta_{c/h}(A|R) := \pm \log \left( \frac{1}{2} + \frac{3}{2\gamma_R^2} \right) \approx \pm 1.5. \]

The qubit \( R \) therefore enables manipulation of energy coherence stored in \( A \) to boost its cooling and heating capabilities. Notice that none of this would be possible without either initial coherence of \( A \) (as demonstrated by no-broadcasting theorems [60, 61]), or without a coherent quantum catalyst (since then the effective channel on \( A \) would be time-symmetric). Moreover, a very similar protocol can be used to demonstrate this effect for all values of \( \beta \) (see Fig. 2). In this case the preprocessing step is applied, and one only needs to tune the initial state of the reference frame so that \( \sigma_R = \omega_R \) still holds.

Motivated by this example we can extend the setup by introducing a reference frame \( R = (H_R, \omega_R) \), so that the energy-preserving interaction \( U \) acts on the system \( A \), the thermometer \( B \) and the reference \( R \) (see Fig. 1d). We do not restrict the reference frame’s state, however, we only allow for interactions that do not modify its state, ensuring the newly introduced system is not a source of non-equilibrium in itself. This is equivalent to quantum catalysis, a phenomenon that has been applied in multiple frameworks [32–37, 59–65]. Contrary to the usual understanding of catalysis, however, here the main purpose of the catalyst is enabling a local violation of the time-translation symmetry on the system \( A \).

The total state subject to the interaction \( U \) is \( \sigma'_{ABR} := U(\rho_A \otimes \gamma_B \otimes \omega_R)U^\dagger \), and the heat becomes \( Q_R(T, H_B, U) := \text{Tr}[H_B(\sigma'_{B} - \gamma_B)] \) with \( \sigma'_{B} = \text{Tr}_{AR} \sigma'_{ABR} \). The catalytic cold temperature is then defined as the effective temperature optimized over all possible reference frames under the catalytic constraint, i.e.

\[
T^c(\sigma_A(\mu), \delta) := \min_{H_B, U, R, \omega_R} T
\]

s.t. \( Q_R(T, H_B, U) \leq -\delta; \)

\[
[U, H_A + H_R + H_B] = 0,
\]

\[
\text{Tr}_{SB} \left[ U(\rho_S \otimes \gamma_B \otimes \omega_R)U^\dagger \right] = \omega_R.
\]

The definition for \( T^c_h(A, \mu) \) is found similarly as before, i.e. by replacing \( \max \) with \( \min \), reversing the side of the inequality and changing \( \delta \to -\delta \). In Appendix C we connect the above problem with the asymptotic setting and find that

\[
T^c_{c/h}(A, \delta) = T^c_{c/h}(A, \delta). \quad (20)
\]

The catalytic effective temperatures therefore recover their asymptotic counterparts. The important difference is that, in the current case, system \( A \) is microscopic and hence \( \delta \) quantifies the total transferred heat, rather than heat per particle. The best possible temperatures \( T^c_{c/h} \) are achieved only when infinitely large systems are used as reference frames. Moreover, when system \( A \) is coherent in the energy basis, the optimal catalyst is necessarily coherent in the energy basis. By limiting ourselves to arbitrarily large but incoherent catalysts we obtain expressions similar to Eqs. (20), with \( \rho_A \) replaced by a dephased state \( D(\rho_A) := \sum_i \vert \epsilon_i \rangle \langle \epsilon_i \vert \rho_A \vert \epsilon_i \rangle \langle \epsilon_i \vert \).

### III. DISCUSSION

In this work we proposed an operational definition of temperature for non-equilibrium quantum systems. Taking inspiration from the Zeroth Law of thermodynamics, we defined two effective temperatures that quantify the intrinsic ability of a quantum state to generate a flow of heat when coupled to a thermal environment (thermometer). We showed that these effective temperatures are given by the maximal and minimal virtual temperatures of the system and connected them with the effective temperature \( T^c \) in the asymptotic limit. We then extended this setting by allowing for the use of coherent reference frames, and found that energy coherences can both increase and decrease the effective temperature, therefore actively influencing the transfer of heat. This implies that quantum coherence plays an important role in generating desired flows of heat in quantum systems and highlights the importance of using suitable reference frames in the study of quantum effects in thermodynamics.

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More precisely, they become indistinguishable for physically relevant local observables. Furthermore, mild conditions are required for $\rho$ and $H$, as illustrated by well-known counterexamples such as integrable systems [66, 67] and many-body localisation [68–70].
Appendix A: Effective temperatures of single-copy quantum systems

We focus on the effective temperature \( T_c(A) \) as the analysis for the complementary case \( T_h(A) \) is similar. Conservation of energy in the form of \( [U, H_A + H_B] = 0 \) implies \( Q(T, H_B, U) = \text{tr}[H_A(\rho_S - \mathcal{E}_T(\rho_S))] \), and so Eq. (6) can be written as

\[
T_c(A) := \min_{\mathcal{E}_T} T \\
\text{s.t.} \quad \text{Tr}[H_A(\mathcal{E}_T(\rho_A) - \rho_A)] > 0, \\
[U, H_A + H_B] = 0. \tag{A1}
\]

In the above we used the fact that optimization over Hamiltonians \( H_B \) and energy-preserving unitaries \( U \) is by definition equivalent to optimizing over all quantum channels of the form (7). This is a well-studied class of quantum channels known as thermal operations [33, 47, 48]. We will often use this correspondence to simplify the expressions for effective temperatures.

The commutation relation \( [U, H_A + H_B] = 0 \) imposes strong limitations on the evolution of quantum states. These restrictions can be conveniently understood using the notion of Bohr spectrum. That is, for a given Hamiltonian \( H \), \( \epsilon \) and \( \lambda \) we define the Bohr spectrum \( \Omega(H) \) to be the set of transition frequencies \( \omega \in \Omega(H) \) such that \( \omega = \epsilon_i - \epsilon_j \) for some \( \epsilon_i, \epsilon_j \in \mathcal{E}(H) \). Consequently, any density operator \( \rho \) can be written as

\[
\rho = \sum_{\omega \in \Omega(H)} \rho(\omega), \tag{A2}
\]

where \( \rho(\omega) \) are called modes of coherence [71, 72]. It can be verified that \( [U, H_A + H_B] = 0 \) implies that the effective channels of the form (7) are symmetric under time translations, that is \( e^{-iHt}\mathcal{E}_\beta(\rho)e^{iHt} = \mathcal{E}_\beta(e^{-iHt}\rho e^{iHt}) \) holds for all \( t \). An important property of such channels is that each mode of coherence evolves independently, which allows to formulate the constraints imposed by unitarity and energy-conservation on quantum evolution in terms of independent transformation laws for each mode [71]. In other words, \( \mathcal{E}_T(\rho) = \sigma \) for some channel \( \mathcal{E}_T \) if and only if

\[
\mathcal{E}_T(\rho(\omega)) = \sigma(\omega) \quad \text{for all} \quad \omega \in \Omega(H). \tag{A3}
\]

Although it is notoriously difficult to characterize how different modes \( \rho(\omega) \) evolve under \( \mathcal{E}_T \) [48, 73], the conditions for transforming the zeroth mode \( \rho(0) \), i.e. the diagonal of \( \rho \) in the basis of \( H \), have been fully characterized [47]. This will be enough for our purposes, and we will express these conditions using Gibbs-stochastic matrices, i.e stochastic matrices \( G_T \) that satisfy \( G_T g = g \) for \( g = \text{diag}(\gamma(T, H_A)) \) being a vector of Gibbs weights [41]. Such matrices characterize energy flows induced by channels \( \mathcal{E}_T \) and provide partial information about the effective dynamics on the system.

Denoting \( p = \text{diag}(\rho_A(0)) \) we can observe that \( \text{Tr}[H_A\mathcal{E}_T(\rho_A)] = \text{Tr} [H_A\mathcal{E}_T(\rho_A^{(0)})] \) and consequently

\[
\text{Tr}[H_A(\mathcal{E}_T(\rho_A) - \rho_A)] = \mathcal{E}(H_A)^T G_T p, \tag{A4}
\]

where \( \mathcal{E}(H) \) should be viewed as a vector of eigenvalues of \( H \). The effective temperature \( T_c(A) \) can be then written as

\[
T_c(A) := \min_{\mathcal{E}_T} T \\
\text{s.t.} \quad \mathcal{E}(H_A)^T (G_T - 1)p > 0, \\
G_T \quad \text{is Gibbs-stochastic.} \tag{A5}
\]

Similarly we can write the expression for the effective temperature \( T_h(A) \) as

\[
T_h(A) := \max_{\mathcal{E}_T} T \\
\text{s.t.} \quad \mathcal{E}(H_A)^T (G_T - 1)p < 0, \\
G_T \quad \text{is Gibbs-stochastic.} \tag{A6}
\]

For any quantum system \( A \) we define the virtual temperature spectrum (VTS) to be the set

\[
\mathbb{V}(A) = \{ T_{ij} | 1 \leq i, j \leq d_A \text{ and } \langle i|H_A|i\rangle \neq \langle j|H_A|j\rangle \}, \tag{A7}
\]

where \( T_{ij} := (\epsilon_j - \epsilon_i)/\log(p_i/p_j) \) with \( \epsilon_i := \langle i|H_A|i\rangle \).

Let us now denote the minimal element of \( \mathbb{V}(A) \) with \( T_{\text{min}} \). First we will show that \( T_c(A) \geq T_{\text{min}} \), i.e. there is no system \( B \) that can be cooled down using system \( A \) when \( T \) is smaller than the minimal virtual temperature of \( A \). Then we will construct
an explicit protocol that allows a qubit thermometer to be cooled as long as $T$ is larger than the minimal virtual temperature of $A$, showing that $T_c(A) \leq T_{\text{min}}$. This will prove that $T_{\text{min}} = T_c(A)$ and solve the problem from Eq. (A5).

To prove the lower bound we note that the condition $T < T_{\text{max}}$ implies $\mathbf{\lambda}(H)^T \mathbf{p} \geq \mathbf{\lambda}(H)^T \mathbf{p}$ for all Gibbs-stochastic matrices $G$. To see this, let us introduce a matrix $M$ with elements $M_{ij}$ such that $G_{ij} = M_{ij} e^{-\beta(\epsilon_j - \epsilon_i)}$. Consider

$$\mathbf{\lambda}(H)^T \mathbf{G} \mathbf{p} = \sum_{i,j} p_i G_{ij} \epsilon_j = \sum_{i,j} p_i M_{ij} e^{-\beta(\epsilon_j - \epsilon_i)} \epsilon_j \leq \sum_{i,j} p_i M_{ij} e^{-\beta \epsilon_j} \epsilon_j = \sum_{i,j} p_j M_{ij} \epsilon_j. \quad (A8)$$

By construction matrix $M$ preserves the identity vector, i.e. $\sum_i M_{ij} = 1$, which follows from the Gibbs-stochastic property of $G$. This allows us to write

$$\sum_{i,j} p_j M_{ij} \epsilon_j = \sum_{i,j} p_j \epsilon_j = \mathbf{\lambda}(H)^T \mathbf{p}. \quad (A9)$$

In other words, when all virtual temperatures are higher than $T$, the system is in a state with the maximal energy possible under all energy-preserving interactions with any thermal state. Consequently, it is impossible to further increase its energy, or cool any thermometer, meaning that $T_c(A) \geq T_{\text{max}}$ as claimed.

To prove the lower bound, suppose that $T_{\text{min}}$ corresponds to energy levels $i$ and $j$, that is $T_{\text{min}} = (\epsilon_j - \epsilon_i) / \log(p_i / p_j).$ Consider the thermometer $B = (H_B, H_B, \gamma_B)$ to be a qubit with $H_B = \text{diag}(0, \Delta)$ and $\gamma_B = \text{diag}(g_0, g_1)$, where $\Delta = \epsilon_j - \epsilon_i$ and $g_0 = (1 + e^{-\beta \Delta})^{-1} = 1 - g_1$. The unitary $U$ is chosen to be a swap between degenerate energy levels, i.e.

$$|\epsilon_i)_A \otimes |1\rangle_B \leftarrow U \rightarrow |\epsilon_j)_A \otimes |0\rangle_B. \quad (A10)$$

This unitary can be generated by a time-independent interaction Hamiltonian $H_{\text{int}} = |\epsilon_i\rangle \langle \epsilon_i|_A + |1\rangle \langle 0|_B + \text{c.c.}$ It can be verified that $U$ changes thermometer’s occupations as $(g_0, g_1) \rightarrow (g_0 + \delta_{ij}, g_1 - \delta_{ij})$ with $\delta_{ij} := p_i g_0 e^{-\beta \Delta} (1 - e^{-\beta \Delta}).$ Therefore, as long as $T \geq T_{\text{min}}$ we have $\delta_{ij} > 0$ and cooling can be achieved, leading to $T_c(A) \leq T_{\text{min}}$ as claimed.

We found the explicit solution to the optimization problem (A5). The proof for the effective hot temperature $T_h(A)$ proceeds identically, so we omit it here. To summarize, for a quantum system $A = (H_A, \rho_A)$ with a virtual temperature spectrum $\nu(A) = \{T_{ij}\}_{i \neq j}$, the effective temperatures are given by

$$T_c(A) = \min \nu(A) = \max_{(i,j): \ i \neq j} T_{ij}, \quad (A11)$$

$$T_h(A) = \max \nu(A) = \min_{(i,j): \ i \neq j} T_{ij}. \quad (A12)$$

Appendix B: Effective temperatures of macroscopic quantum systems

In this Appendix we solve the optimization problem defining effective temperatures of quantum systems processed collectively. We then prove the form of expansions with respect to parameter $\delta$. Since the reasoning for both $T_c^{\infty}(A, \delta)$ and $T_h^{\infty}(A, \delta)$ is completely analogous, we focus on the former.

1. Solution of the problem defining $T_c^{\infty}(A, \delta)$.

The effective temperature $T_c^{\infty}(A, \delta)$ is given by

$$T_c^{\infty}(A, \delta) := \lim_{n \to \infty} T_c(A^n, n\delta) = \lim_{n \to \infty} \min_{\epsilon_f} T \quad \text{s.t.} \quad \text{Tr}[H_A^{\otimes n} (\mathcal{E}_T(\rho_A^{\otimes n}) - \rho_A^{\otimes n})] \geq n \delta, \quad [U, H_A^{\otimes n} + H_B] = 0, \quad (B1)$$

We want to show that the optimal solution of the above problem is exactly the same as the solution to the much simpler problem

$$\min_{\sigma_A} T \quad \text{s.t.} \quad \text{Tr}[H_A(\sigma_A - \rho_A)] \geq \delta, \quad (B2)$$

$$F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A), \quad (B3)$$

$$F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A), \quad (B4)$$
where \( F(\rho, H) := \text{Tr}[\rho H] - T S(\rho) \) is the non-equilibrium free energy. Then we will show that the equivalent problem (B2) can be solved explicitly.

We begin by showing that for any \( n \in \mathbb{N} \) the constraints

\[
\begin{align*}
    &\text{Tr} \left[ U, H_A^\otimes n + H_B \right] = 0, \\
    &\text{Tr} \left[ H_A^\otimes n (E_T(\gamma^\otimes n_A) - \rho_A^\otimes n_A) \right] \geq n \delta,
\end{align*}
\]

imply \( F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A) \) for any \( H_B \) and \( U \). To see this, notice that the unitary invariance of von Neumann entropy implies

\[
\Delta S_S + \Delta S_B \geq 0.
\]

Since \( \Delta S_B = -\beta \Delta E_S - D(\rho'_B\|\gamma_B) \leq -\beta \Delta E_S \), we can write

\[
F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A).
\]

Let us now assume

\[
F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A),
\]

\[
\text{Tr}[H_A(\sigma_A - \rho_A)] \geq \delta
\]

We shall prove that for sufficiently large \( n \in \mathbb{N} \) there always exist a choice of operators \( H_B \) and \( U \) that achieves the optimum \( T_v(A^n, n\delta) \).

Before we proceed we adapt the key result from Ref. [33] that provides a partial asymptotic characterisation of channels \( \mathcal{E}_T \).

**Lemma 1** (Brandao et. al. [33]). Let \( \rho_A \) be an arbitrary density matrix and \( \sigma_A \) be an arbitrary block-diagonal density matrix. Then, for any \( \epsilon > 0 \) there is an \( n \in \mathbb{N} \), a system \( B = (H_B, \gamma_B(H_B, T)) \) and a unitary \( U \) satisfying \( [U, H_A^\otimes n + H_B] = 0 \) and implementing a quantum channel \( \mathcal{E}_T(\cdot) := \text{Tr}_B \left[ U(\cdot \otimes \gamma_B(H_B, T))U^\dagger \right] \) such that

\[
\| \mathcal{E}_T(\rho_A^\otimes n) - \sigma_A^\otimes n \|_1 \leq \epsilon
\]

if and only if \( F_T(\rho_A, H) \geq F_T(\sigma_A, H) \). Moreover, \( \epsilon \) can be taken to be \( \sim O(e^{-\alpha n}) \) for some \( \alpha \in \mathbb{R} \).

In other words, our assumption (B9) implies that for a sufficiently large \( n \) there always exist a thermometer system \( B = (H_B, \gamma_B(H_B, T)) \) and an energy-conserving unitary \( U \) that implements a channel \( \mathcal{E}_T \) such that \( \mathcal{E}_T(\rho_A^\otimes n) \) is arbitrarily close to \( \sigma_A^\otimes n \) and \( F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A) \). This implies that the second line of constraints in Eq. (B1) is satisfied. Moreover, the second assumption (B10) implies that for any \( n \in \mathbb{N} \)

\[
\text{Tr}[H_A^\otimes n (\sigma_A^\otimes n - \rho_A^\otimes n)] \geq n \delta.
\]

Moreover, Eq. (B11) implies that \( \mathcal{E}_T(\rho_A^\otimes n) \geq \sigma_A^\otimes n - \epsilon \gamma^\otimes n_A \) and therefore we have that for \( n \) large enough

\[
\text{Tr}[H_A^\otimes n (\mathcal{E}_T(\rho_A^\otimes n) - \rho_A^\otimes n)] \geq \text{Tr}[H_A^\otimes n (\sigma_A^\otimes n - \rho_A^\otimes n)] - n \epsilon \text{Tr}[H_A] \]

\[
\geq n \delta - O(ne^{-\alpha n}).
\]

Therefore, for a sufficiently large \( n \), the second term vanishes and we recover the first line of constraints in Eq. (B1). This means that the two problems, i.e. (B1) and (B2–B4) have the same solutions.

Now we will show that the solution of the problem (B2) is given by

\[
T_{opt} = \frac{\delta}{S(\gamma_A(E + \delta)) - S(\rho_A)}
\]

where \( \gamma_A(E + \delta) := e^{-\beta^*(E+\delta)H_A}/Z^*(E + \delta) \) with \( Z^*(E + \delta) := \text{Tr} e^{-\beta^*(E+\delta)H_A} \) and \( \beta^*(E + \delta) \) is chosen such that the following implicit relation is satisfied

\[
\text{Tr}[H_A \rho_A] + \delta = \text{Tr}[H_A \gamma_A(E + \delta)].
\]

To prove that Eq. (B15) describes the solution to our simplified problem (B2) we choose a potentially sub-optimal guess for the state \( \sigma_A \), i.e. \( \sigma_A = \gamma_A(E + \delta) \). It is easy to verify that this choice is feasible and achieves the value from Eq. (B15). To see that this is the minimal value achievable under the constraints, notice that any feasible state \( \sigma_A \) must satisfy both

\[
T \geq \frac{\delta}{S(\sigma_A) - S(\rho_A)} \quad \text{and} \quad \text{Tr}[H_A \sigma_A] \geq \text{Tr}[H_A \rho_A] + \delta.
\]

Notice that the optimal \( T \) is always positive. In order to maximize \( S(\sigma_A) \) we further note that Gibbs states have maximal entropy for a given energy. Since for Gibbs states with non-negative temperature entropy decreases with average energy, it is best to choose \( \text{Tr}[H_A \sigma_A] = \text{Tr}[H_A \rho_A] + \delta \). Therefore, we conclude that Eq. (B15) is the solution to our initial problem.
2. The form of $T_c^\infty(A, \delta)$ and $T_h^\infty(A, \delta)$ for small $\delta$.

Let us now expand the effective temperatures for small values of $\delta$. We start by expanding the von Neumann entropy

$$S(\gamma_A(E + \delta)) := S(\gamma_A(E + \delta)) = S(\gamma_A(E)) + \frac{\partial S(\gamma_A(E))}{\partial E} \delta + \frac{1}{2} \frac{\partial^2 S(\gamma_A(E))}{\partial^2 E} \delta^2 + \mathcal{O}(\delta^3). \tag{B18}$$

Plugging this expression into the formula for $T_c^\infty(A, \delta)$ yields

$$\beta_c(A, \delta) = \frac{S(\gamma_A(E)) - S(\rho_A)}{\delta} = \frac{\partial S(\gamma_A(E))}{\partial E} \delta + \frac{1}{2} \frac{\partial^2 S(\gamma_A(E))}{\partial^2 E} \delta + \mathcal{O}(\delta^2). \tag{B19}$$

In order to find the derivatives of $S(\gamma_A(E))$ with respect to $E$ notice that we have

$$\frac{\partial \log Z^*(E)}{\partial E} = \frac{\partial \log Z^*(E)}{\partial \beta^*(E)} \frac{\partial \beta^*(E)}{\partial E} = -E \frac{\partial \beta^*(E)}{\partial E}. \tag{B20}$$

Moreover, differentiating both sides of $\text{Tr}[H_A \gamma^*(\beta^*, E)] = E$ with respect to $E$ we find

$$\frac{\partial \beta^*(E)}{\partial E} = -\frac{1}{E}. \tag{B21}$$

Using the above expressions we can write

$$\frac{\partial S(\gamma_A(E))}{\partial E} = E \frac{\partial \beta^*(E)}{\partial E} + \beta^*(E) + \frac{\partial \log Z^*(E)}{\partial E} = \beta^*(E), \tag{B22}$$

$$\frac{\partial^2 S(\gamma_A(E))}{\partial^2 E} = \frac{\partial \beta^*(E)}{\partial E} = -\frac{1}{E^2}. \tag{B23}$$

Plugging in the above into our expression from Eq. (B19) gives the desired result.

Appendix C: Catalytic effective temperatures $T_c^\infty(A, \delta)$ and $T_h^\infty(A, \delta)$

In this Appendix we show that the catalytic effective temperatures defined in Eq. (19) can be expressed as stated in Eqs. (20). Notice that to prove this, it is enough to show that the optimal solution of the original problem is the same as the solution to the simplified problem defined in Eqs. (B2–B4).

We begin by first showing that the constraints

$$Q_R(T, H_B, U) \leq -\delta \tag{C1}$$

$$\text{Tr}[U, H_A + H_R + H_B] = 0, \tag{C2}$$

$$\text{Tr}_S[B(U(\rho S \otimes \omega_R \otimes \gamma_B)U)^{\dagger}] = \omega_R, \tag{C3}$$

imply that $F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A)$ for any $H_B, H_R, U$ and $\omega_R$. To see this notice that, similarly as before, the unitary invariance of von Neuman entropy implies

$$\Delta S_S + \Delta S_R + \Delta S_B \geq 0. \tag{C4}$$

Our constraints imply $\Delta S_R = 0$ and $\Delta S_B = -\beta \Delta E_S - D(\rho_B\|\gamma_B) \leq -\beta \Delta E_S$, and therefore we obtain

$$F_T(\rho_A, H_A) \geq F_T(\sigma_A, H_A), \tag{C5}$$

which is valid for any choice of operators $H_B, H_R, U$ and $\omega_R$. Moreover, the constraints also imply that $\Delta E_S + \Delta E_B = 0$ and therefore

$$\text{Tr}[H_A(\sigma_A - \rho_A)] \geq \delta. \tag{C6}$$

Let us now assume that Eqs. (C5) and (C6) hold. We want to prove that there always exist feasible operators $H_B, H_R, U$ and $\omega_R$ that achieve the same optimal value as in Eq. (B2–B4). Let us consider

$$\omega_R^n = \frac{1}{n} \sum_{i=1}^{n-1} (\rho^{\otimes n} \otimes \sigma^{\otimes n-i})_{R_A} \otimes |i\rangle\langle i|_{R_M}, \quad H_R = H_{R_A}^{\otimes n-1} \otimes 1_{R_M}, \tag{C7}$$
where we denote \( R = R_A R_M, H_{RA} = H_A, \sigma_n^{-i} := \Tr_{1:i}[\sigma^n] \) with \( \Tr_{1:i}[\cdot] \) denoting the partial trace over the first \( i \) particles and \( \sigma^n \) an arbitrary \( n \)-partite density matrix which we will soon specify. The unitary \( U \) is chosen to be

\[
U := U_{ARB} = W_{AR} \left( \sum_{i=1}^{n} U_{ARB}^{(i)} \otimes |i\rangle_{R_M} \right),
\]

where \( \{U^{(i)}\} \) is a collection of unitaries chosen such that \( U^{(i)} = 1^n \otimes 1_B \) for \( 1 \leq i < n \) and \( U^{(n)} = V \) which we will specify later. The unitary \( W_{AR} \) is a cyclic permutation in the sense that:

\[
W_{AR} [ |i_1\rangle_A \otimes (|i_2\rangle \otimes \ldots \otimes |i_n\rangle)_R ] = |i_n\rangle_A \otimes (|i_1\rangle \otimes \ldots \otimes |i_{n-1}\rangle)_R \otimes |i+1\rangle_{R_M},
\]

with \( |n+1\rangle_{R_M} \equiv |1\rangle_{R_M} \). Up to this point we still need to specify \( H_B, V \) and \( \sigma^n \). Notice that \( U \) leads to the global state

\[
s_{ARB} = U (\rho_A \otimes \omega_R \otimes \gamma_B) U^\dagger
\]

with \( \sigma_{ARB} := Tr_B s_{ARB} \) of the form

\[
s_{ARB} = \frac{1}{n} \Tr_B \left[ W_{AR} (\rho_A \otimes \sigma_{RA}^{\otimes n-1} \otimes \gamma_B \otimes |1\rangle_{RM} + \ldots + \Tr_B [V (\rho_{ARB}^{\otimes n} \otimes \gamma_B) V^\dagger] \otimes |n\rangle_{RM}) W_{AR}^\dagger \right].
\]

Notice that \( U \) is energy-preserving as long as \( V \) is energy-preserving on its support. By the assumption (B3) and Lemma 1 we know that for any \( \epsilon > 0 \) there is a sufficiently large \( n \), a system \( B = (H_B, \gamma_B) \) and energy-preserving unitary \( V \) acting on the subspace \( ARAB \) such that

\[
\left\| \Tr_B [V (\rho_{ARB}^{\otimes n} \otimes \rho_B) V^\dagger] - \sigma^{\otimes n}_{ARB} \right\|_1 \leq \epsilon.
\]

As indicated by the notation, we choose the unitary from Eq. (C11) to be the unitary used in the catalytic protocol (see Eq. (C10)) and our thermometer system \( B \) to be the environment system whose existence is assured by Lemma 1. This assures that \( U \) is energy-conserving, i.e. Eq. (C2) holds. Finally, the density matrix \( \sigma^n \) is chosen to be

\[
\sigma^n := \mathcal{E}_T (\rho_{ARB}^{\otimes n}) = Tr_B \left[ V (\rho_{ARB}^{\otimes n} \otimes \rho_B) V^\dagger \right].
\]

With these identifications we find

\[
s_{ARB} = \frac{1}{n} \left( \sigma_{ARB}^{\otimes n} \otimes |1\rangle_{RM} + \sum_{i=2}^{n} (\rho_{i\otimes i-1}^{\otimes n} \otimes \sigma_{RA}^{\otimes n-i})_{ARB} \otimes |i\rangle_{RM} \right).
\]

A simple calculation further shows that

\[
\Tr_A [\sigma_{ARB}] = \omega_R, \quad \|\sigma_{ARB} - \sigma_A \otimes \omega_R\| \leq \mathcal{O}(\epsilon),
\]

i.e. Eq. (C3) is satisfied and moreover, the protocol generates arbitrarily small correlations between the catalyst \( R \) and system \( A \). Moreover, denoting with \( \Tr_{\bar{i}}(\cdot) \) the partial trace over systems \( \{1, \ldots, i-1, i+1, \ldots, n\} \) we can verify that \( \Tr_R \sigma_{ARB} = \sigma_A \) reads

\[
\sigma_A = \frac{1}{n} \sum_{i=1}^{n} \Tr_{\bar{i}}(\rho_{A}^{\otimes n}).
\]

By our construction \( \mathcal{E}_T (\rho_{A}^{\otimes n}) \) is close to \( \sigma_{A}^{\otimes n} \), with \( \sigma \) being any state satisfying \( F_T (\rho, H_A) \geq F_T (\sigma, H_A) \). Using again the fact that \( \mathcal{E}(\rho_{A}^{\otimes n}) \geq \sigma_{A}^{\otimes n} - \epsilon \1^n \otimes \sigma_{A}^{\otimes n} \) and \( \epsilon \propto \mathcal{O}(\epsilon^{-an}) \), we obtain

\[
\Tr [H_A (\sigma_A - \rho_A)] = \frac{1}{n} \sum_{i=1}^{n} \Tr [H_A (\Tr_{\bar{i}}(\rho_{A}^{\otimes n}) - \rho_A)]
\]

\[
= \frac{1}{n} \Tr [H_A (\mathcal{E}_T (\rho_{A}^{\otimes n}) - \rho_{A}^{\otimes n})]
\]

\[
\geq \Tr [H_A (\sigma_{A}^{\otimes n} - \rho_{A}^{\otimes n})] - n \epsilon \Tr [H_A]
\]

\[
\geq n \delta - \mathcal{O}(n \epsilon^{-an}).
\]

Since \( Q(T, H_B, U) = -\Tr [H_A (\sigma_A - \rho_A)] \), we recover the final constraint (C1). Therefore, by taking \( n \) sufficiently large, which amounts to considering larger catalytic reference frames in Eq. (C7), the solution of our optimization problem approaches the solution of the simplified problem (B2–B4). In the limit \( n \to \infty \) the two problems therefore achieve the same optimal value of \( T \).