Supplemental Material: Axiomatic relation between thermodynamic and information-theoretic entropies.

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This Supplemental Material aims to give more background information on the context of our work, and we elaborate on its technical details. We first give an introduction to the Lieb-Yngvason framework (Section I), focusing on the aspects relevant for our application. Section II contains a short introduction to the information-theoretic concepts that are important for our work: quantum resource theories and information-theoretic entropy measures. We provide technical details and elaborate on the derivations of our results in Sections III – V.

I. LIEB AND YNGVASON'S AXIOMATIC APPROACH

Lieb and Yngvason have devised an axiomatic approach to derive an entropy function for thermodynamic equilibrium states [1, 2]. Recently, they have extended their approach to a special class of non-equilibrium states [3], which also enables them to make predictions relevant for non-equilibrium thermodynamics. We present a short summary of their approach here, focusing on the details relevant for our application. For further information we refer to the original framework [1–4].

Lieb and Yngvason consider a preorder $\prec$ on a set Γ; physically Γ is the space of all equilibrium states of a thermodynamic system. The ordering of the states expresses the existence of adiabatic processes that convert one state into another: for two states $X,\ Y \in \Gamma$ the ordering $X \prec Y$ means that there exists an adiabatic process transforming the system in state X to the state Y. Note that an adiabatic process is explicitly defined as a process that leaves no trace on the environment except that a weight may have changed its relative position. Such transformations are also known as "work processes" [5]. Mathematically, a preorder is reflexive and transitive, but in contrast to a partial order not antisymmetric; two elements X and $Y \in \Gamma$ that satisfy $X \prec Y$ as well as $Y \prec X$ are not necessarily the same element of the set Γ. Whenever both relations $X \prec Y$ and $Y \prec X$ hold, this is denoted by $Y \sim X$, while $X \prec Y$ but not $Y \prec X$ is denoted $X \prec\prec Y$.

Elements $X_1 \in \Gamma_1$ and $X_2 \in \Gamma_2$ of possibly different Γ_1 and Γ_2 can be composed, physically meaning that they can be considered as one composite system before any interaction takes place. The composed state is formally denoted as $(X_1,\ X_2) \in \Gamma_1 \times \Gamma_2$. Note that the Cartesian product $\Gamma_1 \times \Gamma_2$ stands for the space of all states $(X_1,\ X_2)$ of the composed system, where the composition operation is associative and commutative. Furthermore, any element $X \in \Gamma$ can be scaled, i.e., for any $\lambda \in \mathbb{R}_{\geq 0}$ one can define a scaled element denoted as $\lambda X \in \lambda\Gamma$.[1] Scaling a system by a factor λ means taking λ times the amount of substance contained in the original system.

The order relation $\prec$ satisfies by assumption the following six axioms E1 to E6 as well as the Comparison Hypothesis.

- Reflexivity (E1): $X \sim X$.
- Transitivity (E2): $X \prec Y$ and $Y \prec Z \Rightarrow X \prec Z$.
- Consistent composition (E3): $X \prec Y$ and $X' \prec Y'$ $\Rightarrow (X,\ X') \prec (Y,\ Y')$.
- Scaling invariance (E4): $X \prec Y \Rightarrow \lambda X \prec \lambda Y$, $\forall\ \lambda > 0$.
- Splitting and recombination (E5): For $0 < \lambda < 1$, $X \sim (\lambda X,\ (1-\lambda)X)$.
- Stability (E6): If $(X,\ \varepsilon Z_0) \prec (Y,\ \varepsilon Z_1)$ for a sequence of scaling factors $\varepsilon \in \mathbb{R}$ tending to zero, then $X \prec Y$.
- Comparison Hypothesis: Any two elements in a set $(1-\lambda)\Gamma \times \lambda\Gamma$ with $0 \leq \lambda \leq 1$ are related by $\prec$ [2].

The above axioms also directly imply the so called cancellation law [1, 2]: Let X, Y, and Z be any states, then

$$(X,\ Z) \prec (Y,\ Z)\ \Rightarrow\ X \prec Y. \tag{1}$$

Systems in equilibrium can thus not be used to enable state transformations between the states X and Y.

Lieb and Yngvason's contribution concerns possible "entropy functions". More precisely, they show that there is a (essentially) unique real valued function S on the space of all equilibrium states of thermodynamic systems that satisfies the following:

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[1] The scaling is required to obey $1X = X$ as well as $\lambda_1(\lambda_2 X) = (\lambda_1\lambda_2)X$. For the sets Γ, the required properties are $1\Gamma = \Gamma$ and $\lambda_1(\lambda_2\Gamma) = (\lambda_1\lambda_2)\Gamma$, where $\lambda\Gamma$ denotes the space of scaled elements λX.

[2] Note that Lieb and Yngvason do not adopt the Comparison Hypothesis as an axiom but rather derive it from additional axioms about thermodynamic systems [1, 2].

- Additivity: For any two states $X \in \Gamma$ and $X' \in \Gamma'$, $S((X, X')) = S(X) + S(X')$.
- Extensivity: For any $\lambda > 0$ and any $X \in \Gamma$, $S(\lambda X) = \lambda S(X)$.
- Monotonicity: For two states X and $Y \in \Gamma$, $X \prec Y \Leftrightarrow S(X) \leq S(Y)$.

Lieb and Yngvason's second law is rephrased in the following theorem.

Theorem 1 (Lieb & Yngvason)**.** *Provided that the six axioms E1 to E6 as well as the Comparison Hypothesis are fulfilled, there exists a function S that is additive under composition, extensive in the scaling and monotonic with respect to $\prec$. Furthermore, this function S is unique up to an affine change of scale $C_1 \cdot S + C_0$ with $C_1 > 0$.*

For a state $X \in \Gamma$, the unique function S is given as

$$S(X) = \sup \{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\} \quad (2)$$
$$= \inf \{\lambda : X \prec ((1-\lambda)X_0, \lambda X_1)\}, \quad (3)$$

where the elements $X_0 \prec\prec X_1 \in \Gamma$ may be chosen freely, and change the function $S(X)$ only by an affine transformation as stated in the theorem. In this sense, the states X_0, X_1 define a gauge.

The expressions (2) and (3) assume that $X_0 \prec X \prec X_1$, and yield a value $S(X)$ which is between zero and one. However it is straightforward to extend this definition to states X with $X \prec X_0$ or $X_1 \prec X$. Indeed, following the idea in Ref. [2], the expression

$$((1-\lambda)X_0, \lambda X_1) \prec X \quad (4)$$

is equivalent for any $\lambda' \geqslant 0$ to $(((1-\lambda)X_0, \lambda X_1), \lambda' X_1) \prec (X, \lambda' X_1)$ and hence $((1-\lambda)X_0, (\lambda'+\lambda)X_1) \prec (X, \lambda' X_1)$. This allows us to consider negative λ (while still using only positive coefficients as scaling factors). If $\lambda < 0$, by choosing $\lambda' = -\lambda$, the condition (4) is to be understood as $((1-\lambda)X_0) \prec (X, |\lambda| X_1)$. If $\lambda > 1$, following a similar argument, the condition $((1-\lambda)X_0, \lambda X_1) \prec X$ should be understood as $\lambda X_1 \prec ((\lambda-1)X_0, X)$. The same reasoning holds for the expression in (3).

Since the scaling is continuous, the supremum in (2) and the infimum in (3) are attained, and the function S can be conveniently expressed as

$$S(X) = \{\lambda : ((1-\lambda)X_0, \lambda X_1) \sim X\}. \quad (5)$$

The framework described above for equilibrium states can be extended to include non-equilibrium states [3]. To describe non-equilibrium states of a thermodynamic system, additional elements that do not have to satisfy the scaling property are introduced. By adding such non-scalable elements to the set Γ one obtains an extended set Γ_{ext} for which the following is required:

- N1: For any $X' \in \Gamma_{\text{ext}}$ there exist X_0 and $X_1 \in \Gamma$ with $X_0 \prec X' \prec X_1$.
- N2: Axioms E1, E2, E3, and E6, where Z_0 and $Z_1 \in \Gamma$ in axiom E6, hold on Γ_{ext}.

The first requirement ensures that the non-scalable elements are comparable to at least two elements X_0 and X_1 of the set Γ. Furthermore, it assures that the non-scalable elements are not at the boundary of the extended set Γ_{ext} with respect to the preorder $\prec$. For such non-equilibrium states, the following holds [3].

Proposition 2 (Lieb & Yngvason)**.** *On condition that N1 and N2 hold for any non-equilibrium state $X \in \Gamma_{\text{ext}}$, the two functions S_- and S_+ defined as*

$$S_-(X) = \sup \{S(X') : X' \in \Gamma, X' \prec X\}, \quad (6)$$
$$S_+(X) = \inf \{S(X'') : X'' \in \Gamma, X \prec X''\} \quad (7)$$

bound all possible extensions S_{ext} of S to the set Γ_{ext} that are monotonic with respect to $\prec$.

This implies that for any state $X \in \Gamma_{\text{ext}}$, the attained value $S_{\text{ext}}(X)$ of such an extension lies between the values $S(X')$ and $S(X'')$ of its neighboring scalable states according to the order relation $\prec$:

$$S_-(X) \leq S_{\text{ext}}(X) \leq S_+(X).$$

We will prefer to work with the following alternative quantities instead, which only rely on the state X and not on any neighboring equilibrium states X' and X'':

$$\tilde{S}_-(X) = \sup \{\lambda : ((1-\lambda)X_0, \lambda X_1) \prec X\}, \quad (8)$$
$$\tilde{S}_+(X) = \inf \{\lambda : X \prec ((1-\lambda)X_0, \lambda X_1)\}. \quad (9)$$

Operationally, $\tilde{S}_-$ specifies the portion of the system that can maximally be in state X_1 if one wants to create the state X by composing subsystems in states X_0 and X_1. The minimal portion of X_1 that can be obtained by transforming X into a composition of two smaller systems in states X_0 and X_1 is characterized by $\tilde{S}_+$. [3] These new entropic bounds are thus not just characterising a position of the non-equilibrium states within the ordered set of equilibrium states but they have an operational significance. The non-equilibrium states are considered based on the same processes as the equilibrium states, namely with monotonic quantities defined analogous to (2) and (3). Note that in thermodynamics the two sets of bounding quantities $\{S_-, S_+\}$ and $\{\tilde{S}_-, \tilde{S}_+\}$ coincide, as due to the continuity of the thermodynamic quantities an equilibrium state $X' \in \Gamma$ with $X' \sim ((1-\lambda)X_0, \lambda X_1)$ exists for any λ. The two sets of bounds only differ if there are $\tilde{\lambda}$ such that the composed systems $((1-\tilde{\lambda})X_0, \tilde{\lambda} X_1)$ cannot be reversibly inter-converted with an equilibrium state, meaning that there does not exist a state $\tilde{X} \in \Gamma$ such that $\tilde{X} \sim ((1-\tilde{\lambda})X_0, \tilde{\lambda} X_1)$. In this case the interval

[3] Note that if a state X does not obey $X_0 \prec X \prec X_1$ the definitions are consistently extended like (2) and (3).

$[\tilde{S}_-, \tilde{S}_+]$ may be smaller than $[S_-, S_+]$; the former may not contain all possible monotonic extensions S_{ext} of the entropy function S. On the other hand, it may allow for a distinction of non-equilibrium states that lie between the same pair of equilibrium states. Thus, depending on the application one or the other set of bounding quantities may be preferred. We will see in Section III that the quantities $\tilde{S}_-$ and $\tilde{S}_+$ appear natural in our microscopic setting. The following lemma confirms that the quantities (8) and (9) always lead to the same necessary as well as essentially the same sufficient conditions for state transformations as (6) and (7).

Lemma 3. *Let $X,\ Y \in \Gamma_{\text{ext}}$. Then, the following two conditions hold:*

$$\tilde{S}_+(X) < \tilde{S}_-(Y) \Rightarrow X \prec Y, \tag{10}$$

$$X \prec Y \Rightarrow \tilde{S}_-(X) \leq \tilde{S}_-(Y) \text{ and } \tilde{S}_+(X) \leq \tilde{S}_+(Y). \tag{11}$$

Note that (10) and (11) have been shown to hold for S_- and S_+ in Ref. [3]. The following proof proceeds similarly.

Proof. To show (10), let $\tilde{S}_+(X) < \tilde{S}_-(Y)$. Then there exist $\lambda < \lambda'$ such that $X \prec ((1-\lambda)X_0,\ \lambda X_1)$ and $((1-\lambda')X_0,\ \lambda' X_1) \prec Y$, where $X_0 \prec\prec X_1 \in \Gamma$. With E5 we can rewrite

$$((1-\lambda)X_0,\ \lambda X_1) \sim ((1-\lambda')X_0,\ (\lambda'-\lambda)X_0,\ \lambda X_1)$$

as well as

$$((1-\lambda')X_0,\ \lambda' X_1) \sim ((1-\lambda')X_0,\ (\lambda'-\lambda)X_1,\ \lambda X_1).$$

According to E4, $X_0 \prec X_1$ implies $(\lambda'-\lambda)X_0 \prec (\lambda'-\lambda)X_1$. With E3, the above relations imply

$$((1-\lambda)X_0, \lambda X_1) \prec ((1-\lambda')X_0, \lambda' X_1).$$

Thus by transitivity (E2) $X \prec Y$.

For (11), observe that if $((1-\lambda)X_0, \lambda X_1) \prec X$ and $X \prec Y$, then according to E2 also $((1-\lambda)X_0, \lambda X_1) \prec Y$. This implies that $\tilde{S}_-(X) \leq \tilde{S}_-(Y)$. Similarly, $Y \prec ((1-\lambda')X_0, \lambda' X_1)$ and $X \prec Y$, thus $X \prec ((1-\lambda')X_0, \lambda' X_1)$ and $\tilde{S}_+(X) \leq \tilde{S}_+(Y)$. □

Note that in the case of a continuous entropy function S on Γ, supremum and infimum in the definition of $\tilde{S}_-$ and $\tilde{S}_+$ are attained, which implies that in (10) the strict inequality can be replaced by $\leq$. This is in particular satisfied in thermodynamics. For the quantum resource theories considered later supremum and infimum are attained for rational entropy values.

II. INTRODUCTION TO QUANTUM RESOURCE THEORIES AND INFORMATION-THEORETIC ENTROPY MEASURES

In general, a resource theory is a means to investigate which tasks can be achieved or how certain states of systems may change, if the processes affecting a system are of a predefined class, often called the *allowed operations*.

To quantify the utility of different states with respect to a given resource theory, values are assigned to them. This is usually achieved with so called *monotones*, functions that are monotonic under the class of allowed operations. Intuitively, monotones quantify the variety of states that can be generated from each state and serve as a means to compare the latter. A state is called a resource if it cannot be prepared with operations from the allowed class only.

For quantum resource theories, the state space on which the allowed operations act is composed of density operators, i.e., positive semi-definite operators of unit trace on a Hilbert space $\mathcal{H}$. We denote the set of all density operators on $\mathcal{H}$ as $\mathcal{S}(\mathcal{H})$ and consider only finite dimensional Hilbert spaces throughout this supplemental material. In the following we introduce the two most prominent quantum resource theories, the resource theories of noisy and thermal operations. Note that log denotes the logarithm with respect to base 2, while ln stands for the natural logarithm throughout this supplemental material.

A. The resource theory of noisy operations

The resource theory of noisy operations [6–8] is defined by the following class of allowed operations:

- composition of the system with an ancillary system in a maximally mixed state;
- reversible transformation on the system and ancilla with any joint unitary;
- partial trace over any subsystem.

For finite dimensional systems, a state $\rho \in \mathcal{S}(\mathcal{H})$ can be transformed into a state $\tilde{\rho} \in \mathcal{S}(\mathcal{H})$ by noisy operations if and only if ρ majorizes $\tilde{\rho}$ [6].

Definition 4. *Let $\rho,\ \tilde{\rho} \in \mathcal{S}(\mathcal{H})$ with $d = \dim \mathcal{H}$ and eigenvalues $p_1 \geq p_2 \geq \ldots \geq p_d$ and $\tilde{p}_1 \geq \tilde{p}_2 \geq \ldots \geq \tilde{p}_d$. The state ρ **majorizes** the state $\tilde{\rho}$, denoted as $\rho \prec_{\text{M}} \tilde{\rho}$* [4]*,*

[4] To avoid confusion with Lieb and Yngvason's order relation later, we use a non-standard notation for the majorization relation $\prec_{\text{M}}$, which in particular differs from the notational convention used in [9].

iff for all $k \in \{1, 2, \ldots, d\}$

$$\sum_{i=1}^{k} p_i \geq \sum_{i=1}^{k} \tilde{p}_i,$$

with equality for $k = d$.

The spectrum of a state ρ with ordered eigenvalues $p_1 \geq p_2 \geq \ldots \geq p_d$ can be represented as a step function,

$$f_\rho(x) = \begin{cases} p_i, & i-1 \leq x \leq i, \\ 0, & \text{otherwise.} \end{cases} \tag{12}$$

Majorization can be equivalently expressed in terms of f_ρ:

$$\rho \prec_{\mathrm{M}} \tilde{\rho} \;\Leftrightarrow\; \int_0^k f_\rho(x)dx \;\geq\; \int_0^k f_{\tilde{\rho}}(x)dx, \quad \forall\, k \in \mathbb{R}_{\geq 0}. \tag{13}$$

As $f_\rho(x)$ is monotonically decreasing in x and due to the normalization $\int_0^\infty f_\rho(x)dx = 1$, the condition $k \in \{1, 2, \ldots, d\}$ from Definition 4 is equivalently replaced with $k \in \mathbb{R}_{\geq 0}$. Noisy operations and majorization are furthermore related to unital operations [8, 10–12].

Definition 5. *A* ***unital*** *quantum operation on $\mathcal{S}(\mathcal{H})$ is a trace preserving completely positive map that preserves the identity operator $\mathbb{1}_{\dim(\mathcal{H})}$.*

Note that a positive map M is completely positive if $M \otimes \mathbb{1}_{\mathbb{C}^{d\times d}}$ is positive for any d, where $\mathbb{1}_{\mathbb{C}^{d\times d}}$ is the identity on $\mathbb{C}^{d\times d}$.

Proposition 6. *For two density operators ρ, $\tilde{\rho} \in \mathcal{S}(\mathcal{H})$ the following are equivalent:*

- *There exists a noisy operation that achieves the transformation $\rho \to \tilde{\rho}$.*
- *There exists a unital quantum operation that achieves the transformation $\rho \to \tilde{\rho}$.*
- *The state ρ majorizes the state $\tilde{\rho}$, denoted $\rho \prec_{\mathrm{M}} \tilde{\rho}$.*

This is proven for instance in [8, 10]. Note that majorization is also tightly related to the resource theory of entanglement [13–16].

The resource theory of noisy operations features numerous monotonic functions [8, 17]. Arguably the most popular monotones are the Rényi entropies [18].

Definition 7. *The* ***α-Rényi entropy*** *of a density operator $\rho \in \mathcal{S}(\mathcal{H})$ is defined as*

$$H_\alpha(\rho) := \frac{1}{1-\alpha} \log \operatorname{tr}(\rho^\alpha).$$

The limit $\alpha \to 1$ yields the von Neumann entropy $H(\rho) = -\operatorname{tr}(\rho \log \rho)$. Furthermore, for $\alpha \to \infty$ and $\alpha = 0$ we recover two quantities from the smooth entropy framework, the min-entropy, $H_{\min}$, and the max-entropy, $H_{\max}$ [19, 20].

Definition 8. *For a density operator $\rho \in \mathcal{S}(\mathcal{H})$ its* ***min and max-entropies*** *are*

$$H_{\min}(\rho) := -\log \|\rho\|_\infty, \tag{14}$$

$$H_{\max}(\rho) := \log \operatorname{rank} \rho, \tag{15}$$

where $\|\rho\|_\infty$ denotes the maximal eigenvalue of ρ.[5]

B. The resource theory of thermal operations

The resource theory of thermal operations describes quantum systems interacting with a thermal environment at a temperature T [25–27]. The allowed operations in this framework are:

- composition with an ancillary system (of arbitrary Hamiltonian) in a thermal state relative to the heat bath at temperature T;
- reversible and energy-conserving transformation of the system and the ancilla;
- removal of any subsystem.

Thermal states, also called Gibbs states, are of the form

$$\tau = \sum_i \frac{e^{-\beta E_i}}{Z} |E_i\rangle \langle E_i|, \tag{16}$$

where Z is the partition function and the $\{|E_i\rangle\}_i$ are the energy eigenstates of a corresponding Hamiltonian H; the constant $\beta = \frac{1}{k_{\mathrm{B}}T}$ is inversely proportional to the temperature T and k_{B} denotes the Boltzmann constant. These states are preserved under thermal operations, while all athermal states are resource states [27, 28]. In the above definition the energy levels may be degenerate. In the extreme case of a system with a trivial Hamiltonian, i.e., a system where all energy levels are degenerate, the resource theory of thermal operations is equivalent to the resource theory of noisy operations.

Closely connected to the resource theory of thermal operations is the order relation of thermo-majorization, which may be defined in terms of a rescaled step function [27, 29].

Definition 9. *Let $\rho \in \mathcal{S}(\mathcal{H})$ be a density matrix that is block diagonal in the energy eigenbasis and let $d = \dim \mathcal{H}$.*

[5] This definition of the max-entropy corresponds to the one in Ref. [19], and differs from that in Refs. [20–23]. The former is the Rényi entropy of order zero, while the latter is the Rényi entropy of order 1/2. Note, however, that all Rényi entropies with $\alpha < 1$ attain similar values (after smoothing) [24], and the term "max-entropy" should be understood as designating this class of similar measures.

Represent its spectrum as in (12)*. The* ***Gibbs-rescaled step function*** *of* ρ *is*

$$f_\rho^{\mathrm{T}}(x) = \begin{cases} \frac{p_i}{e^{-\beta E_i}}, & \sum_{k=1}^{i-1} e^{-\beta E_k} \leq x \leq \sum_{k=1}^{i} e^{-\beta E_k}, \\ 0, & \textit{otherwise}, \end{cases}$$

where the eigenvalues are reordered such that $\frac{p_1}{e^{-\beta E_1}} \geq \frac{p_2}{e^{-\beta E_2}} \geq \ldots \geq \frac{p_d}{e^{-\beta E_d}}$*;* E_i *denotes the* i*-th energy eigenvalue.*[6]

Thermo-majorization may be defined in terms of Gibbs-rescaled step functions, analogous to the formulation of majorization in (13).

Definition 10. *Let* ρ *and* $\sigma \in \mathcal{S}(\mathcal{H})$ *be two quantum states that are both block diagonal in the energy eigenbasis. The order relation of* ***thermo-majorization****,* $\prec_{\mathrm{T}}$*, is defined as*

$$\rho \prec_{\mathrm{T}} \sigma \;\Leftrightarrow\; \int_0^k f_\rho^{\mathrm{T}}(x)dx \;\geq\; \int_0^k f_\sigma^{\mathrm{T}}(x)dx, \quad \forall\, k \in \mathbb{R}_{\geq 0}.$$

Note that this definition is equivalent to the one in [27]. Furthermore, for block diagonal states in the energy eigenbasis, thermal operations can be characterized in terms of $\prec_{\mathrm{T}}$ [27].

Proposition 11 (Horodecki & Oppenheim)**.** *Let* ρ *and* $\sigma \in \mathcal{S}(\mathcal{H})$ *be two states that are block diagonal in the energy eigenbasis.* [7] *Then there exists a thermal operation that achieves the transformation* $\rho \to \sigma$ *iff the state* ρ *thermo-majorizes the state* σ*, denoted* $\rho \prec_{\mathrm{T}} \sigma$*.* [8]

As shown in [28], a family of measures that are monotonic under thermal operations[9] for block diagonal states ρ and for all $\alpha \geq 0$ are

$$F_\alpha(\rho) := k_{\mathrm{B}} T D_\alpha(\rho||\tau)\ln(2) + F(\tau),$$

where τ is the thermal state of the system, Z_τ is its partition function, and $F(\tau) := -k_{\mathrm{B}} T \ln Z_\tau$ is its free energy. For commuting states ρ and τ, the Rényi divergences $D_\alpha(\rho||\tau)$ for $\alpha \geq 0$ are

$$D_\alpha(\rho||\tau) := \frac{1}{\alpha - 1} \log \sum_i p_i^\alpha t_i^{1-\alpha},$$

where p_i are the eigenvalues of ρ and t_i are the eigenvalues of τ. These measures include the $F_{\min}$ for $\alpha = 0$ and the $F_{\max}$ in the limit $\alpha \to \infty$:

$$F_{\min}(\rho) := k_{\mathrm{B}} T D_0(\rho||\tau)\ln(2) + F(\tau), \tag{17}$$

$$F_{\max}(\rho) := k_{\mathrm{B}} T D_\infty(\rho||\tau)\ln(2) + F(\tau). \tag{18}$$

Note that $D_0(\rho||\tau) = -\log \operatorname{tr} \Pi_\rho \tau$, where Π_ρ is the projector onto the support of ρ, and $D_\infty(\rho||\tau) = \log \min\{\lambda : \rho \leq \lambda\tau\}$ correspond to the relative entropies with respect to the thermal state of the system [21, 30]. For a thermal state all F_α coincide.

The two quantities $F_{\min}$ and $F_{\max}$ were originally introduced to describe the extractable work as well as the work needed to form a state [27]. Assuming no errors for these two processes and that the states $\rho \in \mathcal{S}(\mathcal{H})$ are block-diagonal in the energy eigenbasis, the extractable work under thermal operations is

$$W_{\mathrm{ext}} = F_{\min}(\rho) - F_{\min}(\tau),$$

whereas the work of formation is

$$W_{\mathrm{form}} = F_{\max}(\rho) - F_{\max}(\tau).$$

In the thermodynamic limit the extractable work of a state $\rho \in \mathcal{S}(\mathcal{H})$ is

$$W(\rho) = F(\rho) - F(\tau);$$

the same quantity is used to describe the work of formation [27].

III. APPLICATION TO MICROSCOPIC SYSTEMS

The axiomatic framework introduced in Section I was explicitly devised for macroscopic systems considered from the perspective of phenomenological thermodynamics. We describe these systems from a microscopic viewpoint based on the same axiomatic approach. Section III A gives additional details on our microscopic model, while Section III B elaborates on the proof of Proposition 1 from the main text.

A. Description of our microscopic model

In our model, the set of states Γ_{ext} consists of all density operators on a Hilbert space $\mathcal{S}(\mathcal{H})$. All our considerations are restricted to finite dimensional Hilbert spaces $\mathcal{H}$. The subset of "equilibrium states", Γ, is defined as comprising those states with a uniform spectrum, i.e., for which all non-zero eigenvalues are equal.

We express the adiabatic processes (as introduced in the main text and detailed also in Section I) by concrete physical operations that consist of the following steps:

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[6] Note that several energy eigenvalues may be identical.

[7] Note that unitary operations that commute with the Hamiltonian are free operations. They allow for the inter conversion of such states with the corresponding diagonalised ones.

[8] Note that the result in [27] is actually more general: it also applies to initial states ρ which are not block diagonal in the energy eigenbasis, as long as the final states are. A thermal operation $\rho \to \sigma$ is then equivalent to an ordering $\rho_{\mathrm{dec}} \prec_{\mathrm{T}} \sigma$, where ρ_{dec} denotes the state ρ decohered in the energy eigenbasis. The reason for this is that thermal operations commute with a decohering operation in the energy eigenbasis, which is mathematically a projection of the state onto its energy eigenspaces. Therefore, the transitions $\rho_{\mathrm{dec}} \to \sigma$ is equivalent to $\rho \to \sigma_{\mathrm{dec}} = \sigma$.

[9] Note that [28] derived monotonicity for the more general class of thermal operations with catalysis. The results on monotonicity carry over to the subset of thermal operations.

- composition with an extra ancilla system in an "equilibrium state";
- reversible and energy-preserving interaction of the system and the ancilla with a weight system;
- removal of the ancilla, whose final reduced state must be the same as its initial state.

We denote such processes with the symbol $\xrightarrow{A}$.

As in Lieb and Yngvason's axiomatic framework, there is no restriction on the size of the ancillary system; it may be an environment that is larger than the system of interest and it may even be macroscopic. The ancilla is removed by tracing it out, where its reduced state has to coincide with its initial one. Thus, the ancilla system, if probed, looks unchanged. No effect is observed by looking at the system's environment (except for the change in the weight system detailed in the following).

The interaction with the weight implements any unitary transformation on the system and the ancilla. An explicit model of the weight introduced in Ref. [31] represents the idea of an adiabatic process particularly well. The weight system W in question has a Hamiltonian

$$H_{\mathrm{W}} := s \sum_{w} w \left|w\right\rangle \left\langle w\right|$$

corresponding to an energy ladder, where the $\{|w\rangle\}_w$ are orthonormal states and the constant $s \in \mathbb{R}_{\geq 0}$ defines the energy level spacing of the Hamiltonian. The weight, assumed to be in a state $\sigma = |\eta_{\mathrm{L,l_0}}\rangle \langle \eta_{\mathrm{L,l_0}}|$ with $|\eta_{\mathrm{L,l_0}}\rangle = \frac{1}{\sqrt{L}} \sum_{w=0}^{L-1} |w + l_0\rangle$, is connected to a quantum system SA with Hamiltonian H_{SA} (in our case SA consists of the system and the ancilla). The operations on the system and the weight commute with the weight's translation along the ladder, independently of its absolute energetic state. Only the relative change in energy of the weight, which also corresponds to the energy that is added to or removed from the system and the ancilla, influences the latter. These operations furthermore conserve the total energy of system, ancilla, and weight combined, in the sense that they commute with $H_{\mathrm{SA}} \otimes \mathbb{1}_{\mathrm{W}} + \mathbb{1}_{\mathrm{SA}} \otimes H_{\mathrm{W}}$, where H_{SA} is the Hamiltonian on system and ancilla and H_{W} is the Hamiltonian of the weight [31, 32]. For large L, i.e., for a sufficiently coherent state, these operations on the system SA and the weight allow for the implementation of any unitary operation on SA. The interaction with the weight thus reduces to the application of arbitrary unitaries to the system and the ancilla, using the weight system catalytically.

We emphasize that our considerations are, however, not restricted to this particular weight model. For instance in Ref. [33], an arbitrary potential that is switched on for a time interval is considered instead of an explicit weight system. This model also leads to arbitrary unitary dynamics.

The weight system effectively eliminates the role of energy from the processes on the system and the ancilla or, alternatively, allows us to change their Hamiltonian at will. It is thus not altogether surprising, that the above processes $\xrightarrow{A}$ resemble the noisy operations introduced in Section II A. However, they allow the composition with any equilibrium ancilla yet require us to return the ancillas to their initial state. The following lemma shows that these processes are also characterized by the majorization relation, and, that they are thus equivalent to noisy operations in the sense that they allow for the same state transformations.

Lemma 12. *For two states ρ, $\sigma \in \mathcal{S}(\mathcal{H}_{\mathrm{S}})$ the following are equivalent:*

- *(A): The spectrum of ρ majorizes the spectrum of σ, i.e., $\rho \prec_{\mathrm{M}} \sigma$.*
- *(B): There exists a process $\rho \xrightarrow{A} \sigma$.*

Proof. (A) $\Rightarrow$ (B): If $\rho \prec_{\mathrm{M}} \sigma$, then there exists a noisy operation bringing ρ to σ [6], i.e., there exists a unitary U_{SA} acting on an additional ancillary system A such that

$$\mathrm{tr}_{\mathrm{A}} \left(U_{\mathrm{SA}} \left(\rho \otimes \frac{\mathbb{1}_{\mathrm{A}}}{\dim(\mathcal{H}_{\mathrm{A}})} \right) U_{\mathrm{SA}}^{\dagger} \right) = \sigma,$$

where $\frac{\mathbb{1}_{\mathrm{A}}}{\dim(\mathcal{H}_{\mathrm{A}})} \in \mathcal{S}(\mathcal{H}_{\mathrm{A}})$ is a maximally mixed ancilla and $U_{\mathrm{SA}}^{\dagger}$ denotes the adjoint of U_{SA}. Note that noisy operations allow for the composition with ancilla systems A of arbitrary dimension. In the original proof of this, Horodecki and Oppenheim construct particular operations, for which the unitary U_{SA} does not change the reduced state on the ancillary system, i.e.,

$$\mathrm{tr}_{\mathrm{S}} \left(U_{\mathrm{SA}} \left(\rho \otimes \frac{\mathbb{1}_{\mathrm{A}}}{\dim(\mathcal{H}_{\mathrm{A}})} \right) U_{\mathrm{SA}}^{\dagger} \right) = \frac{\mathbb{1}_{\mathrm{A}}}{\dim(\mathcal{H}_{\mathrm{A}})}.$$

Thus, the ancilla is traced out in the maximally mixed state in which it was added and the process is an adiabatic process $\rho \xrightarrow{A} \sigma$ according to our definition.

(B) $\Rightarrow$ (A): As stated in Proposition 6, $\rho \prec_{\mathrm{M}} \sigma$ is equivalent to the existence of a unital map from ρ to σ. In the following, we show that the processes $\rho \xrightarrow{A} \sigma$ are unital and thus also imply the ordering $\rho \prec_{\mathrm{M}} \sigma$. Now let $\chi \in \mathcal{S}(\mathcal{H}_{\mathrm{A}})$ be a state with a flat spectrum, i.e., it can be written as $\chi = \sum_{l=1}^{d} \frac{1}{d} |l\rangle \langle l|$ with $d \leq \dim(\mathcal{H}_{\mathrm{A}})$. Our operations $\xrightarrow{A}$ are the subset of the operations $\mathrm{tr}_{\mathrm{A}}(U_{\mathrm{SA}}((\cdot) \otimes \chi) U_{\mathrm{SA}}^{\dagger})$ acting on a state ρ, for which the partial trace removes the reduced state χ, i.e., $\mathrm{tr}_{\mathrm{S}} \left(U_{\mathrm{SA}} \left(\frac{\mathbb{1}}{\dim(\mathcal{H}_{\mathrm{S}})} \otimes \chi \right) U_{\mathrm{SA}}^{\dagger} \right) = \chi$; U_{SA} denotes an arbitrary unitary.

Consider the function $h(\rho) = -\mathrm{tr}(\rho \log \rho)$.[10] For the

[10] Note that even though this function corresponds to the von Neumann entropy, we regard it as a purely mathematical function

maximally mixed state $\rho = \frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})}$ the following holds,

$$\begin{aligned} h(\rho \otimes \chi) &= h\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) \\ &= h\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right) \\ &\leq h\left(\mathrm{tr}_\mathrm{A}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right)\right) \\ &\quad + h\left(\mathrm{tr}_\mathrm{S}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right)\right). \end{aligned} \tag{19}$$

The inequality follows by subadditivity of h. Furthermore, we know that

$$h\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) = \log(\dim(\mathcal{H}_\mathrm{S}) \cdot d).$$

Since the ancillary system has to be in state χ at the end of the process,

$$h\left(\mathrm{tr}_\mathrm{S}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right)\right) = \log d.$$

From (19) we conclude that

$$h\left(\mathrm{tr}_\mathrm{A}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right)\right) \geq \log \dim(\mathcal{H}_\mathrm{S}).$$

Note that $\mathrm{tr}_\mathrm{A}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right) \in \mathcal{S}(\mathcal{H})$, as the partial trace itself is a trace preserving and completely positive map. Therefore, the above inequality can only be satisfied if $\mathrm{tr}_\mathrm{A}\left(U_\mathrm{SA}\left(\frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})} \otimes \chi\right) U_\mathrm{SA}^\dagger\right) = \frac{\mathbb{1}}{\dim(\mathcal{H}_\mathrm{S})}$, as otherwise its entropy is smaller. The processes $\xrightarrow{A}$ are thus unital. □

The majorization relation imposes a partial ordering on the set of all quantum states, as required by Lieb and Yngvason's framework. Furthermore, not all quantum states can be compared by means of the majorization relation, thus the latter emerges paired with a notion of comparability that expresses whether two states can be ordered by means of $\prec_\mathrm{M}$.

Recall that for two states ρ, $\tilde{\rho} \in \mathcal{S}(\mathcal{H})$ the majorization condition $\rho \prec_\mathrm{M} \tilde{\rho}$ can be equivalently expressed in terms of the spectral step functions f_ρ and $f_{\tilde{\rho}}$ according to (13). Even though the functions f_ρ are not in one-to-one correspondence with the states $\rho \in \mathcal{S}(\mathcal{H})$ (they rather represent all states with a certain spectrum) this description is sufficient for this purpose.[11]

For an equilibrium state ρ, which, by definition, has a flat spectrum, the step function f_ρ is conveniently written in terms of its rank as

$$f_\rho(x) = \begin{cases} \frac{1}{\mathrm{r}(\rho)}, & 0 \leq x \leq \mathrm{r}(\rho), \\ 0, & \text{otherwise}, \end{cases}$$

with $\mathrm{r}(\rho) := \mathrm{rank}\,\rho$. This notation for the rank is used throughout this section. For two equilibrium states ρ and $\tilde{\rho}$ the rank alone determines which one majorizes the other, as in that case the relation $\rho \prec_\mathrm{M} \tilde{\rho}$ is equivalent to

$$\int_0^k \frac{1}{\mathrm{r}(\rho)} dx \;\geq\; \int_0^k \frac{1}{\mathrm{r}(\tilde{\rho})} dx, \quad \forall\, k \in \mathbb{R}_{\geq 0},$$

and thus to $\mathrm{r}(\rho) \leq \mathrm{r}(\tilde{\rho})$.

We define the composition of two states $\rho \in \mathcal{S}(\mathcal{H})$ and $\tilde{\rho} \in \mathcal{S}(\tilde{\mathcal{H}})$ as their tensor product $\rho \otimes \tilde{\rho} \in \mathcal{S}(\mathcal{H} \otimes \tilde{\mathcal{H}})$. This means that two systems are considered uncorrelated before any interaction takes place. In an interaction correlations between subsystems may be established. Similarly, the ancillary system is assumed to be initially uncorrelated with the system, which can be ensured by choosing ancillas that have not interacted with the system before or that have been decoupled from the system through other interactions. The same view is taken in [27, 34]. The scaling of an equilibrium state ρ is assumed to coincide with its composition for scaling factors $\lambda \in \mathbb{N}$. The step function of a scaled state $\lambda\rho \in \lambda\mathcal{S}(\mathcal{H})$, which is defined as $\rho^{\otimes\lambda} \in \mathcal{S}(\mathcal{H}^{\otimes\lambda})$, is

$$\begin{aligned} f_{\lambda\rho}(x) &= \begin{cases} \left(\frac{1}{\mathrm{r}(\rho)}\right)^\lambda, & 0 \leq x \leq \mathrm{r}(\rho)^\lambda, \\ 0, & \text{otherwise}, \end{cases} \\ &= f_\rho(x^{\frac{1}{\lambda}})^\lambda. \end{aligned}$$

Note that correlations within the system do not affect this scaling operation: From the perspective of an outside observer with the ability to apply adiabatic processes to the system, its internal properties (such as the entanglement of individual particles, for instance) are not accessible. Hence, they may not be incorporated into the observer's description of the system and our considerations escape the potential issues with entanglement in microscopic systems that were raised in [4].

To obtain a continuous scaling operation, this way of scaling the step function is applied for any $\lambda \in \mathbb{R}_{>0}$. For most values of λ the scaled copies $\lambda\rho$ do not represent physical states and no actual space $\lambda\mathcal{S}(\mathcal{H})$ exists. However, any normalized, but possibly unphysical, function

with the mathematical properties that it is subadditive, unitarily invariant, additive for product states, and it reaches its maximum of $\log(\dim(\mathcal{H}))$ iff ρ is maximally mixed. The reason why we consider this quantity is that we know rather well how it behaves; however, any other mathematical function that satisfies these properties could have been used instead.

[11] As the processes $\xrightarrow{A}$ include the application of an arbitrary unitary, states with the same spectra can be inter converted by means of an allowed operation.

$f(x)$, can be turned into a physical state by actually considering the function $\frac{1}{n}f(x/n)$ for a large enough n: this function now effectively describes the state of the system along with an ancilla of dimension n in a fully mixed state. Indeed, we can always combine states with a fully mixed state of a given rank, and the following rules apply:

$$\lambda\left(\rho, \frac{\mathbb{1}_n}{n}\right) \sim \left(\lambda\rho, \frac{\mathbb{1}_{n^\lambda}}{n^\lambda}\right) \ ;$$
$$\left(\left(\rho, \frac{\mathbb{1}_n}{n}\right), \left(\tilde{\rho}, \frac{\mathbb{1}_m}{m}\right)\right) \sim \left((\rho, \tilde{\rho}), \frac{\mathbb{1}_{n\cdot m}}{n\cdot m}\right) \ .$$

These rules are easily verified by representing the states in terms of their step functions. They give physical significance to any relative statements involving states that would be required to be scaled in an unphysical way: for example, $(\lambda\rho, \mu\tilde{\rho}) \prec \sigma$ if and only if $\left(\lambda\left(\rho, \frac{\mathbb{1}_n}{n}\right), \mu\left(\tilde{\rho}, \frac{\mathbb{1}_m}{m}\right)\right) \prec \left(\sigma, \left(\frac{\mathbb{1}_{n^\lambda m^\mu}}{n^\lambda m^\mu}\right)\right)$. Thus, if $\lambda\rho$ does not actually correspond to a physical state, then the second expression should in fact be considered; indeed for large enough n the state $\lambda\left(\rho, \frac{\mathbb{1}_n}{n}\right)$ is physical to a good approximation.

The entropy function (2) can thus be equivalently rewritten as

$$S(\rho) = \sup\left\{\lambda : \left((1-\lambda)\left(\rho_0, \ \frac{\mathbb{1}_n}{n}\right), \ \lambda\left(\rho_1, \ \frac{\mathbb{1}_n}{n}\right)\right) \prec \left(\rho, \ \frac{\mathbb{1}_n}{n}\right)\right\} \ , \tag{21}$$

where the last expression (to a good approximation) only involves physical states for a large enough n.

B. Proof of Proposition 1 from the main text

In order to derive entropy functions for our microscopic model, we first have to show that it obeys Lieb and Yngvason's axioms.

Lemma 13. *Consider the majorization relation $\prec_{\mathrm{M}}$ and the composition and scaling operations defined above. Then, for equilibrium states the six axioms E1 to E6 as well as the Comparison Hypothesis hold. For non-equilibrium states axioms N1 and N2 hold.*

Proof. As axiom N2 requires that axioms E1 to E3 as well as E6 hold for non-equilibrium states, we directly verify them for arbitrary states.

Reflexivity (E1): $\prec_{\mathrm{M}}$ is clearly reflexive: For $\rho \in \mathcal{S}(\mathcal{H})$ and for all $k \in \mathbb{R}_{\geq 0}$,

$$\int_0^k f_\rho(x)dx = \int_0^k f_\rho(x)dx,$$

and thus $\rho \sim_{\mathrm{M}} \rho$.

Transitivity (E2): Let ρ, σ, and $\chi \in \mathcal{S}(\mathcal{H})$. Then, $\rho \prec_{\mathrm{M}} \sigma$ and $\sigma \prec_{\mathrm{M}} \chi$ is equivalent to

$$\int_0^k f_\rho(x)dx \geq \int_0^k f_\sigma(x)dx \geq \int_0^k f_\chi(x)dx, \quad \forall\ k \in \mathbb{R}_{\geq 0}.$$

Thus, $\rho \prec_{\mathrm{M}} \chi$.

Consistent composition (E3): Let $\rho \prec_{\mathrm{M}} \sigma \in \mathcal{S}(\mathcal{H})$ with $d = \dim(\mathcal{H})$ and with eigenvalues $p_1 \geq p_2 \geq \ldots \geq p_d$ and $q_1 \geq q_2 \geq \ldots \geq q_d$ and let $\rho' \prec_{\mathrm{M}} \sigma' \in \mathcal{S}(\mathcal{H}')$ with $d' = \dim(\mathcal{H}')$ and with eigenvalues $p'_1 \geq p'_2 \geq \ldots \geq p'_{d'}$ and $q'_1 \geq q'_2 \geq \ldots \geq q'_{d'}$. Note that the composed state $(\rho, \ \rho')$ with eigenvalues $p''_l = p_i p'_j$ ordered according to $p''_1 \geq p''_2 \geq \ldots \geq p''_{dd'}$ has an associated step function

$$f_{(\rho, \ \rho')}(x) = \begin{cases} p''_l, & l-1 \leq x \leq l, \\ 0, & \text{otherwise}, \end{cases} ,$$

for $l = 1, \ 2, \ \ldots \ , \ dd'$. Then for any $0 \leq k \leq dd'$ we can choose $m_1 \geq m_2 \geq \ldots \geq m_{d'} \geq 0$ with $m_1 + m_2 + \cdots + m_{d'} = k$ such that

$$\sum_{l=0}^{k} p''_l = p_1 \sum_{j=0}^{m_1} p'_j + p_2 \sum_{j=0}^{m_2} p'_j + \cdots + p_d \sum_{j=0}^{m_{d'}} p'_j.$$

This is possible since for any i and j the inequality $p_i p'_j \geq p_i p'_{j+k}$ holds for all $k \geq 0$. Now as $\rho' \prec_{\mathrm{M}} \sigma'$ the inequality

$$\sum_{j=0}^{m_i} p'_j \leq \sum_{j=0}^{m_i} q'_j,$$

holds for any $0 \leq i \leq d'$. Therefore,

$$\begin{aligned} p_1 \sum_{j=0}^{m_1} p'_j + p_2 \sum_{j=0}^{m_2} p'_j + \cdots + p_d \sum_{j=0}^{m_{d'}} p'_j \\ \leq p_1 \sum_{j=0}^{m_1} q'_j + p_2 \sum_{j=0}^{m_2} q'_j + \cdots + p_d \sum_{j=0}^{m_{d'}} q'_j. \end{aligned} \tag{22}$$

Now the terms in (22) can be regrouped with $n_1 \geq n_2 \geq \ldots \geq n_d \geq 0$ obeying $n_1 + n_2 + \cdots + n_d = k$ as

$$\begin{aligned} q'_1 \sum_{j=0}^{n_1} p_j + q'_2 \sum_{j=0}^{n_2} p_j + \cdots + q'_{d'} \sum_{j=0}^{n_{d'}} p_j \\ \leq q'_1 \sum_{j=0}^{n_1} q_j + q'_2 \sum_{j=0}^{n_2} q_j + \cdots + q'_{d'} \sum_{j=0}^{n_{d'}} q_j. \end{aligned}$$

The inequality holds as $\rho \prec_{\mathrm{M}} \sigma$ implies that for any $0 \le i \le d$,

$$\sum_{j=0}^{m_i} p_j \le \sum_{j=0}^{m_i} q_j.$$

Furthermore,

$$q'_1 \sum_{j=0}^{n_1} q_j + q'_2 \sum_{j=0}^{n_2} q_j + \cdots + q'_{d'} \sum_{j=0}^{n_{d'}} q_j \le \sum_{l=0}^{k} q''_l.$$

as the terms in the last sum might be ordered differently. This concludes the proof that $(\rho,\ \rho') \prec_{\mathrm{M}} (\sigma,\ \sigma')$.

Stability (E6): Note that χ_0 and χ_1 are equilibrium states; only for those the scaling operation is defined. Let $\rho \in \mathcal{S}(\mathcal{H})$ have eigenvalues $p_1 \ge p_2 \ge \ldots \ge p_d$ with $d = \dim(\mathcal{H})$. Assume that $(\rho,\ \varepsilon\chi_0) \prec_{\mathrm{M}} (\sigma,\ \varepsilon\chi_1)$ for a sequence of ε's tending to zero. Let this sequence be denoted by $(\varepsilon_i)_i$. Then for all ε_i we have

$$\int_0^k f_{(\rho,\varepsilon_i\chi_0)}(x)dx \ \ge \ \int_0^k f_{(\sigma,\varepsilon_i\chi_1)}(x)dx, \quad \forall\ k \in \mathbb{R}_{\ge 0}.$$

Taking the limit $i \to \infty$ leads to

$$\lim_{i\to\infty} \int_0^k f_{(\rho,\varepsilon_i\chi_0)}(x)dx \ \ge \ \lim_{i\to\infty} \int_0^k f_{(\sigma,\varepsilon_i\chi_1)}(x)dx,$$

$\forall\ k \in \mathbb{R}_{\ge 0}$ and thus

$$\int_0^k \lim_{i\to\infty} f_{(\rho,\varepsilon_i\chi_0)}(x)dx \ge \int_0^k \lim_{i\to\infty} f_{(\sigma,\varepsilon_i\chi_1)}(x)dx,$$

$\forall\ k \in \mathbb{R}_{\ge 0}$, which follows by dominated convergence. Note that

$$f_{(\rho,\varepsilon_i\chi_0)}(x) = \begin{cases} p_l \frac{1}{\mathrm{r}(\chi_0)^{\varepsilon_i}}, & (l-1)\,\mathrm{r}(\chi_0)^{\varepsilon_i} \le x \le l\,\mathrm{r}(\chi_0)^{\varepsilon_i}, \\ 0, & \text{otherwise,} \end{cases}$$

and similarly for $f_{(\sigma,\varepsilon_i\chi_1)}$. Thus, taking the limit leads to

$$\int_0^k f_\rho(x)dx \ \ge \ \int_0^k f_\sigma(x)dx, \quad \forall\ k \in \mathbb{R}_{\ge 0},$$

which is equivalent to $\rho \prec_{\mathrm{M}} \sigma$.

Since for equilibrium states the rank suffices to assert majorization, E4 and E5 as well as the Comparison Hypothesis can be efficiently checked:

Scaling invariance (E4): We see that

$$\begin{aligned} \rho \prec_{\mathrm{M}} \sigma \ &\Leftrightarrow\ \mathrm{r}(\sigma) \ \ge \mathrm{r}(\rho) \\ &\Leftrightarrow\ \mathrm{r}(\sigma)^\lambda \ \ge\ \mathrm{r}(\rho)^\lambda, \quad \forall\ \lambda\ >\ 0 \\ &\Leftrightarrow\ \lambda\rho \prec_{\mathrm{M}} \lambda\sigma, \quad \forall\ \lambda\ >\ 0. \end{aligned}$$

Splitting and recombination (E5): Let $0 < \lambda < 1$. Then,

$$\begin{aligned} f_{(\lambda\rho,(1-\lambda)\rho)}(x) &= \begin{cases} \frac{1}{\mathrm{r}(\rho)^\lambda}\frac{1}{\mathrm{r}(\rho)^{1-\lambda}}, & 0 \le x \le \mathrm{r}(\rho)^\lambda\,\mathrm{r}(\rho)^{1-\lambda}, \\ 0, & \text{otherwise,} \end{cases} \\ &= \begin{cases} \frac{1}{\mathrm{r}(\rho)}, & 0 \le x \le \mathrm{r}(\rho), \\ 0, & \text{otherwise,} \end{cases} \\ &= f_\rho(x). \end{aligned}$$

Comparison Hypothesis: Let $0 \le \lambda \le 1$ and $0 \le \mu \le 1$ and let $\rho,\ \tilde\rho,\ \sigma\ \tilde\sigma \in \mathcal{S}(\mathcal{H})$ be arbitrary equilibrium states. Then the state $(\lambda\rho, (1-\lambda)\sigma)$ with step function

$$f_{(\lambda\rho,(1-\lambda)\sigma)}(x) = \begin{cases} \frac{1}{\mathrm{r}(\rho)^\lambda}\frac{1}{\mathrm{r}(\sigma)^{1-\lambda}}, & 0 \le x \le \mathrm{r}(\rho)^\lambda\,\mathrm{r}(\sigma)^{1-\lambda}, \\ 0, & \text{otherwise,} \end{cases}$$

can be related to any $(\mu\tilde\rho, (1-\mu)\tilde\sigma)$ in the sense of (13).

Axiom (N1): Choose ρ_0 to be a pure state and $\rho_1 = \frac{\mathbb{1}}{\dim(\mathcal{H})}$ maximally mixed. For any state $\rho \in \mathcal{S}(\mathcal{H})$ we know that $\rho_0 \prec_{\mathrm{M}} \rho$ and $\rho \prec_{\mathrm{M}} \rho_1$. □

Corollary 14. *For a system on which processes $\xrightarrow{A}$ can be performed, there exists a unique entropy function S for equilibrium states, as well as bounds S_- and S_+ on the entropy of non-equilibrium states, all up to an affine change of scale.*

Proof. Lemma 13 allows the application of Lieb and Yngvason's Theorem 1 and Proposition 2 to quantum states compared by means of $\prec_{\mathrm{M}}$. This implies the corollary. □

We are now in a position to prove Proposition 1 from the main text.

Proof of Proposition 1 from the main text. For any state $\rho \in \mathcal{S}(\mathcal{H})$ with eigenvalues $p_1 \ge p_2 \ge \ldots \ge p_d$, where $d = \dim \mathcal{H}$, and for any equilibrium states $\rho_0 \prec\prec_{\mathrm{M}} \rho_1$, let λ be such that $((1-\lambda)\rho_0, \lambda\rho_1) \prec_{\mathrm{M}} \rho$. Then,

$$\int_0^k f_{((1-\lambda)\rho_0,\lambda\rho_1)}(x)dx \ge \int_0^k f_\rho(x)dx, \quad \forall\ k \in \mathbb{R}_{\ge 0}. \tag{23}$$

Let $\tilde k = \mathrm{r}(\rho_0)^{1-\lambda}\,\mathrm{r}(\rho_1)^\lambda$. As ρ_0 and ρ_1 are equilibrium states, we know that for $0 \le k \le \tilde k$,

$$\int_0^k f_{((1-\lambda)\rho_0,\lambda\rho_1)}(x)dx = \int_0^k \left(\frac{1}{\mathrm{r}(\rho_0)}\right)^{1-\lambda} \left(\frac{1}{\mathrm{r}(\rho_1)}\right)^{\lambda} dx.$$

Thus, by considering $k \le 1$, Equation (23) directly implies

$$\left(\frac{1}{\mathrm{r}(\rho_0)}\right)^{1-\lambda} \left(\frac{1}{\mathrm{r}(\rho_1)}\right)^{\lambda} \ge p_1, \tag{24}$$

which can be rewritten as

$$C_1 \cdot \log\frac{1}{p_1} + C_0 \ge \lambda, \tag{25}$$

with $C_1 = \frac{1}{\log\frac{\mathrm{r}(\rho_1)}{\mathrm{r}(\rho_0)}}$ and $C_0 = -\frac{1}{\log\frac{\mathrm{r}(\rho_1)}{\mathrm{r}(\rho_0)}}\log \mathrm{r}(\rho_0)$. On the other hand, Equation (24) implies

$$\begin{aligned} \left(\frac{1}{\mathrm{r}(\rho_0)}\right)^{1-\lambda} \left(\frac{1}{\mathrm{r}(\rho_1)}\right)^{\lambda} \min\left\{k, \tilde k\right\} &\ge p_1 \cdot \min\left\{k, \frac{1}{p_1}\right\} \\ &\ge \int_0^k f_\rho(x)dx, \end{aligned}$$

for all $k \in \mathbb{R}_{\geq 0}$, i.e., implies (23); the second inequality follows as the step function $f_\rho(x)$ is monotonously decreasing and normalised. Thus, taking the supremum over λ in (25) concludes the proof for $\tilde{S}_-$, as $H_{\min}(\rho) = -\log \|\rho\|_\infty$, where $\|\rho\|_\infty$ denotes the maximal eigenvalue of the state ρ, i.e., equals p_1.

For $\tilde{S}_+$ we proceed similarly. Let $\rho \in \mathcal{S}(\mathcal{H})$ and let $\rho_0 \prec\prec_{\mathrm{M}} \rho_1$ be two equilibrium states, as above. Now let λ be such that $\rho \prec_{\mathrm{M}} ((1-\lambda)\rho_0, \lambda\rho_1)$ and thus

$$\int_0^k f_{((1-\lambda)\rho_0,\lambda\rho_1)}(x)dx \leq \int_0^k f_\rho(x)dx, \quad \forall\, k \in \mathbb{R}_{\geq 0}. \tag{26}$$

First, we show that

$$\mathrm{r}(\rho_0)^{1-\lambda}\,\mathrm{r}(\rho_1)^\lambda \geq \mathrm{r}(\rho) \tag{27}$$

by contradiction: Assume for now that $\mathrm{r}(\rho_0)^{1-\lambda}\,\mathrm{r}(\rho_1)^\lambda < \mathrm{r}(\rho)$. For $\tilde{k} = \mathrm{r}(\rho_0)^{1-\lambda}\,\mathrm{r}(\rho_1)^\lambda$,

$$\int_0^{\tilde{k}} f_\rho(x)dx < 1.$$

This contradicts (26), as

$$\int_0^{\tilde{k}} f_{((1-\lambda)\rho_0,\lambda\rho_1)}(x)dx = 1.$$

Thus we have $\tilde{k} \geq \mathrm{r}(\rho)$, which can be rewritten as

$$\lambda \geq C_1 \cdot \log \mathrm{r}(\rho) + C_0 \tag{28}$$

with C_1 and C_0 defined as above. Moreover, (27) implies

$$\begin{aligned}\left(\frac{1}{\mathrm{r}(\rho_0)}\right)^{1-\lambda}\left(\frac{1}{\mathrm{r}(\rho_1)}\right)^{\lambda}\min\left\{k,\tilde{k}\right\} &\leq \frac{1}{\mathrm{r}(\rho)}\min\left\{k,\mathrm{r}(\rho)\right\}\\ &\leq \int_0^k f_\rho(x)dx\end{aligned}$$

for all $k \in \mathbb{R}_{\geq 0}$, i.e., implies (26); the second inequality holds as $f_\rho(x)$ is monotonously decreasing and normalised. As $H_{\max}(\rho) = \log \mathrm{r}(\rho)$, taking the infimum over λ in (28) concludes the proof for $\tilde{S}_+$.

In the case of an equilibrium state ρ, for $\lambda = S(\rho)$ the relation $((1-\lambda)\rho_0, \lambda\rho_1) \sim_{\mathrm{M}} \rho$ holds. Note that for these states $\log \mathrm{r}(\rho) = \log \frac{1}{p_1}$. Thus, according to the above considerations,

$$\lambda = C_1 \cdot \log \mathrm{r}(\rho) + C_0,$$

with parameters C_0 and C_1 defined like before. This also coincides with the von Neumann entropy H (up to an affine change of scale). □

In particular, $H_{\min}$ and $H_{\max}$ are exactly recovered for the choice $\mathrm{r}(\rho_0) = 1$ and $\mathrm{r}(\rho_1) = 2$. States obeying $\rho_1 \prec_{\mathrm{M}} \rho$ are associated with a $\lambda > 1$ and thus an entropy larger than 1, interpreted like in Section I.

According to Lemma 3, the information-theoretic entropy measures $H_{\min}$ and $H_{\max}$ obtain an additional meaning as characterising the state transformations by means of adiabatic processes in terms of necessary and sufficient conditions. Note that these entropy measures and thus the $\tilde{S}_-$ and $\tilde{S}_+$ in our particular model have the appealing property that they are additive under the composition of two states $\rho, \sigma \in \mathcal{S}(\mathcal{H})$:

$$\begin{aligned}\tilde{S}_-(\rho \otimes \sigma) &= \tilde{S}_-(\rho) + \tilde{S}_-(\sigma),\\ \tilde{S}_+(\rho \otimes \sigma) &= \tilde{S}_+(\rho) + \tilde{S}_+(\sigma).\end{aligned}$$

Thus, if σ is an equilibrium state,

$$\begin{aligned}\tilde{S}_-(\rho \otimes \sigma) &= \tilde{S}_-(\rho) + S(\sigma),\\ \tilde{S}_+(\rho \otimes \sigma) &= \tilde{S}_+(\rho) + S(\sigma).\end{aligned}$$

As mentioned in Section I, these bounds $\tilde{S}_-$ and $\tilde{S}_+$ may not equal S_- and S_+. With the continuous scaling operation and our understanding of the entropic bounds in the same way as previously explained for the entropy function (21), the two sets of entropic quantities coincide.

This is further illustrated with the following example of a qubit. Let $\rho_0 = |0\rangle\langle 0|$ and $\rho_1 = \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1|$. Consider a qubit in the state $\rho = \frac{3}{4}|0\rangle\langle 0| + \frac{1}{4}|1\rangle\langle 1|$. Now the closest qubit equilibrium state ρ' preceding it in the order is $\rho' = \rho_0$, a state with entropy $S(\rho') = 0$. With the continuous scaling operation, as detailed above, we actually consider

$$\sup\left\{S(\rho') : \left(\rho', \frac{\mathbb{1}}{3}\right) \prec \left(\rho, \frac{\mathbb{1}}{3}\right)\right\} = \log\frac{4}{3},$$

where not ρ' but rather $\left(\rho', \frac{\mathbb{1}}{3}\right)$ is required to be a physical state. This equals

$$\tilde{S}_-(\rho) = \sup\left\{\lambda : ((1-\lambda)\rho_0, \lambda\rho_1) \prec \rho\right\} = \log\frac{4}{3}.$$

Note that we may thus distinguish the state ρ from another state $\sigma = \frac{2}{3}|0\rangle\langle 0| + \frac{1}{3}|1\rangle\langle 1|$ by means of its entropic bounds.

IV. INTERACTION WITH A HEAT BATH

Lieb and Yngvason's framework is based on rather abstract axioms, which admits its application to other physical contexts. In typical laboratory experiments, the systems of interest interact with a thermal environment. Considering systems connected to an external heat reservoir is thus a natural and particularly useful application. In the following, we elaborate on this scenario and prove Proposition 2 from the main text.

States equilibrated with respect to a thermal reservoir at a temperature T are the thermal states of the form (16). As in the case of adiabatic processes, we also consider states that are (normalised) projections of (16) onto a subspace (i.e., states where only a subset of the energy eigenstates are populated) as members of the class of "equilibrium states". Note that the notion of an equilibrium state depends on the Hamiltonian of the system.

The possible state transitions of a system connected to a thermal reservoir at a temperature T are modelled by the resource theory of thermal operations introduced in Section II B. According to Proposition 11 from [27], the ordering of states under these operations is encompassed by means of the order relation of thermo-majorization, as long as the considered states are block-diagonal in the energy eigenbasis.

As equilibrium states are always diagonal in the energy eigenbasis, the relation $\prec_{\mathrm{T}}$ fully captures their inter convertibility. For those non-equilibrium states which are not block diagonal in the energy eigenbasis, the relation $\prec_{\mathrm{T}}$ is not sufficient to express whether two states can be inter converted by thermal operations[12]. In the following, we therefore restrict our treatment to equilibrium states and to non-equilibrium states that are block diagonal in the energy eigenbasis. The following proposition ensures the applicability of Theorem 1 and Proposition 2 to quantum states ordered with $\prec_{\mathrm{T}}$.

Proposition 15. *Consider the order relation of thermo-majorization $\prec_{\mathrm{T}}$. Then, for equilibrium states τ the six axioms E1 to E6 as well as the Comparison Hypothesis hold, whereas all block diagonal non-equilibrium states satisfy axioms N1 and N2.*

By Definition 10, block diagonal states $\rho \in \mathcal{S}(\mathcal{H})$ can be represented by their Gibbs-rescaled step functions f_ρ^{T}. For equilibrium states τ the functions f_τ^{T} take the simple form

$$f_\tau^{\mathrm{T}}(x) = \begin{cases} \frac{1}{Z_\tau}, & 0 \le x \le Z_\tau, \\ 0, & \text{otherwise}, \end{cases}$$

where Z_τ is the partition function on the subspace of τ. We define the composition of two arbitrary states as their tensor product, like before. For scaling factors $\lambda \in \mathbb{N}$ the scaling of an equilibrium state is again assumed to coincide with its composition. This scaling operation can be formally extended to any scaling factor $\lambda \in \mathbb{R}_{>0}$ on the level of the functions f^{T}. The Gibbs-rescaled step function of an equilibrium state $\lambda\tau$ has the form

$$f_{\lambda\tau}^{\mathrm{T}}(x) = \begin{cases} \left(\frac{1}{Z_\tau}\right)^\lambda, & 0 \le x \le Z_\tau^\lambda, \\ 0, & \text{otherwise}. \end{cases}$$

[12] More precisely, $\prec_{\mathrm{T}}$ can only relate such non-equilibrium states to states which are block diagonal in the energy eigenbasis and only as long as the state that is not block diagonal is the preceding element in the order, as was previously mentioned in Section II. Consult [27] for further clarification.

Note that because these functions are flat, we can, similarly to Section III, give a meaning to scaling with non-integer factors λ by considering states on a larger Hilbert space.

The Gibbs-rescaled f_ρ^{T} are normalized and monotonically decreasing like the f_ρ. Furthermore, for equilibrium states τ the partition function on the subspace where they live, Z_τ, fully determines which states thermo-majorize which others. More specifically, for two equilibrium states τ and $\tilde{\tau}$,

$$\begin{aligned} \tau \prec_{\mathrm{T}} \tilde{\tau} \Leftrightarrow \int_0^k f_\tau^{\mathrm{T}}(x)dx \;\ge\; \int_0^k f_{\tilde{\tau}}^{\mathrm{T}}(x)dx, \quad \forall\, k \in \mathbb{R}_{\ge 0} \\ \Leftrightarrow Z_{\tilde{\tau}} \ge Z_\tau. \end{aligned} \tag{29}$$

Thus for the f_ρ^{T} the partition function takes the role of the rank in f_ρ.

Proof of Proposition 15. Substituting the f_ρ with the f_ρ^{T} and the rank with the partition function Z, we can apply the proof of Lemma 13 to prove the axioms E1 to E6 as well as the Comparison Hypothesis for the order relation of thermo-majorization $\prec_{\mathrm{T}}$. Note that when adapting the proof of E3, the choice of the $\{m_i\}_i$ and the $\{n_i\}_i$ is not problematic, as all energies are positive and hence $0 \le e^{-\beta E_i} \le 1$. Furthermore, axiom N1 holds as the spectrum of a state $\rho = \sum_{i,d_i,d_i'} \rho_{i,d_i,d_i'} |E_i,\ d_i\rangle\langle E_i,\ d_i'| \in \mathcal{S}(\mathcal{H})$ always thermo-majorizes $\tau_1 = \sum_{i,d_i} \frac{e^{-\beta E_i}}{Z} |E_i, d_i\rangle\langle E_i, d_i|$ and is thermo-majorized by $\tau_0 = |E_1\rangle\langle E_1|$. The d_i and d_i' account for the degeneracy of each energy level. □

As all axioms are satisfied by the order relation $\prec_{\mathrm{T}}$, Theorem 1 implies that there is a unique entropy function

$$S_{\mathrm{T}}(\rho) = \{\lambda : ((1-\lambda)\tau_0, \lambda\tau_1) \sim_{\mathrm{T}} \tau\},$$

which is additive under composition by means of the tensor product, extensive under the scaling operation and monotonic under thermal operations. There are furthermore bounds on the monotonic extensions of this function to other block-diagonal states.

Proof of Proposition 2 from the main text. Let $\rho \in \mathcal{S}(\mathcal{H})$ be block diagonal with rescaled eigenvalues $p_i^{\mathrm{res}} = \frac{p_i}{e^{-\beta E_i}}$ ordered as $p_1^{\mathrm{res}} \ge p_2^{\mathrm{res}} \ge \ldots \ge p_d^{\mathrm{res}}$ with $d = \dim(H)$ and let $\tau_0 \prec\prec_{\mathrm{T}} \tau_1$ be two equilibrium states. Let λ be such that $((1-\lambda)\tau_0, \lambda\tau_1) \prec_{\mathrm{T}} \rho$. Then,

$$\int_0^k f_{((1-\lambda)\tau_0,\lambda\tau_1)}^{\mathrm{T}}(x)dx \ge \int_0^k f_\rho^{\mathrm{T}}(x)dx, \quad \forall k \in \mathbb{R}_{\ge 0}. \tag{30}$$

As τ_0 and τ_1 are equilibrium states, for any $0 \le k \le Z_{\tau_0}^{1-\lambda} Z_{\tau_1}^{\lambda}$

$$\int_0^k f_{((1-\lambda)\tau_0,\lambda\tau_1)}^{\mathrm{T}}(x)dx = \int_0^k \left(\frac{1}{Z_{\tau_0}}\right)^{1-\lambda}\left(\frac{1}{Z_{\tau_1}}\right)^{\lambda} dx.$$

Therefore, (30) implies

$$\left(\frac{1}{Z_{\tau_0}}\right)^{1-\lambda}\left(\frac{1}{Z_{\tau_1}}\right)^{\lambda} \geq p_1^{\mathrm{res}}, \tag{31}$$

which can be rewritten as

$$a_{\mathrm{T}} \cdot \ln \frac{1}{p_1^{\mathrm{res}}} + b_{\mathrm{T}} \geq \lambda. \tag{32}$$

with $a_{\mathrm{T}} = \frac{1}{\ln \frac{Z_{\tau_1}}{Z_{\tau_0}}}$ and $b_{\mathrm{T}} = -a_{\mathrm{T}} \cdot \ln Z_{\tau_0}$ depending on the gauge states τ_0 and τ_1. On the other hand, (31) implies

$$\left(\frac{1}{Z_{\tau_0}}\right)^{1-\lambda}\left(\frac{1}{Z_{\tau_1}}\right)^{\lambda} \min\left\{k, \tilde{k}\right\} \geq p_1^{\mathrm{res}} \cdot \min\left\{k, \frac{1}{p_1^{\mathrm{res}}}\right\} \geq \int_0^k f_\rho^{\mathrm{T}}(x)dx,$$

for all $k \in \mathbb{R}_{\geq 0}$; the second inequality holds as $f_\rho^{\mathrm{T}}(x)$ is monotonously decreasing and normalised. Hence, conditions (30) and (31) are equivalent.

For a state ρ that is block diagonal in the energy eigenbasis

$$\begin{aligned} F_{\max}(\rho) &= -k_{\mathrm{B}}T \ln Z_\tau + k_{\mathrm{B}}T D_\infty(\rho||\tau)\ln(2) \\ &= -k_{\mathrm{B}}T \ln Z_\tau + k_{\mathrm{B}}T \ln \min\{\lambda : \rho \leq \lambda\tau\} \\ &= k_{\mathrm{B}}T \ln \min\{\mu : \rho \leq Z_\tau \mu\tau\} \\ &= k_{\mathrm{B}}T \ln p_{\max}^{\mathrm{res}}, \end{aligned}$$

where $p_{\max}^{\mathrm{res}}$ is the maximal rescaled eigenvalue of the state ρ. Thus, taking the supremum over λ in (32) implies that $\tilde{S}_{\mathrm{T}-}(\rho) = F_{\max}(\rho)$ up to affine change of scale.

For $\tilde{S}_{\mathrm{T}+}$ the proof works similarly. Let $\rho \in \mathcal{S}(\mathcal{H})$ and let $\tau_0 \prec\!\prec_T \tau_1$ be two equilibrium states. Now let λ be such that $\rho \prec_{\mathrm{T}} ((1-\lambda)\tau_0, \lambda\tau_1)$ and thus

$$\int_0^k f^{\mathrm{T}}_{((1-\lambda)\tau_0,\lambda\tau_1)}(x)dx \leq \int_0^k f_\rho^{\mathrm{T}}(x)dx, \quad \forall\, k \in \mathbb{R}_{\geq 0}. \tag{33}$$

First we show by contradiction that

$$Z_{\tau_0}^{1-\lambda} Z_{\tau_1}^{\lambda} \geq Z_\rho. \tag{34}$$

Assume for now that $Z_{\tau_0}^{1-\lambda} Z_{\tau_1}^{\lambda} < Z_\rho$. For $\tilde{k} = Z_{\tau_0}^{1-\lambda} Z_{\tau_1}^{\lambda}$ we therefore find

$$\int_0^{\tilde{k}} f_\rho^{\mathrm{T}}(x)dx < 1.$$

This contradicts (33) as

$$\int_0^{\tilde{k}} f^{\mathrm{T}}_{((1-\lambda)\tau_0,\lambda\tau_1)}(x)dx = 1.$$

Thus we have $\tilde{k} \geq Z_\rho$, which can be rewritten as

$$\lambda \geq a_{\mathrm{T}} \cdot \ln Z_\rho + b_{\mathrm{T}}, \tag{35}$$

with a_{T} and b_{T} defined as above. Moreover, (34) implies

$$\left(\frac{1}{Z_{\tau_0}}\right)^{1-\lambda}\left(\frac{1}{Z_{\tau_1}}\right)^{\lambda} \min\left\{k, Z_{\tau_0}^{1-\lambda} Z_{\tau_1}^{\lambda}\right\} \leq \frac{1}{Z_\rho} \min\left\{k, Z_\rho\right\} \leq \int_0^k f_\rho^{\mathrm{T}}(x)dx,$$

for all $k \in \mathbb{R}_{\geq 0}$, i.e., it implies (33); the second inequality holds as $f_\rho^{\mathrm{T}}(x)$ is monotonously decreasing and normalized.

Furthermore, we find that

$$\begin{aligned} F_{\min}(\rho) &= -k_{\mathrm{B}}T \ln Z_\tau + k_{\mathrm{B}}T D_0(\rho||\tau)\ln(2) \\ &= -k_{\mathrm{B}}T \ln Z_\tau - k_{\mathrm{B}}T \ln \operatorname{tr} \Pi_\rho \tau \\ &= -k_{\mathrm{B}}T \ln \left(Z_\tau \operatorname{tr} \Pi_\rho \tau\right) \\ &= -k_{\mathrm{B}}T \ln Z_\rho, \end{aligned}$$

where Π_ρ denotes the projector onto the support of ρ, as before. Taking the infimum over λ in (35) implies that $\tilde{S}_{\mathrm{T}+}(\rho) = F_{\min}(\rho)$ up to affine change of scale and concludes the proof for $\tilde{S}_{\mathrm{T}+}$.

For an equilibrium state τ and for $\lambda = S_{\mathrm{T}}(\tau)$ the relation $((1-\lambda)\tau_0, \lambda\tau_1) \sim_{\mathrm{T}} \tau$ holds. Furthermore, $\ln Z_\tau = \ln \frac{1}{p_{\max}^{\mathrm{res}}}$ holds for such states. Hence, according to the above considerations,

$$\lambda = a_{\mathrm{T}} \cdot \ln Z_\tau + b_{\mathrm{T}}.$$

This concludes the proof. □

The function $S_{\mathrm{T}}(\tau)$ equals the Helmholtz free energy

$$F(\tau) = -k_{\mathrm{B}}T \ln Z_\tau$$

up to an affine change of scale and a factor -1.[13] This additional factor reflects that F is not monotonically increasing but rather decreasing under thermal operations.

That the quantities $\tilde{S}_{\mathrm{T}-}$ and $\tilde{S}_{\mathrm{T}+}$ calculated within our axiomatic approach are related to the work of formation $F_{\max}$ as well as to the extractable work $F_{\min}$ from [27], is perhaps not surprising, since both approaches employ the tools of majorization and thermo-majorization.

V. INTERACTION WITH OTHER TYPES OF RESERVOIRS

Adding other reservoirs to a physical system leads to mathematically equivalent situations, even though the underlying physics differs. Here, we outline the two other scenarios from Table I of the main text.

[13] Note that one would require two gauge states with partition functions $Z_{\tau_0} = 1$ and $Z_{\tau_1} = e^{-\beta}$ to formally recover $S_{\mathrm{T}}(\tau) = F(\tau)$. This choice of parameters, however, would obey $\tau_1 \prec\!\prec_{\mathrm{T}} \tau_0$ and not the required $\tau_0 \prec\!\prec_{\mathrm{T}} \tau_1$.

A. Interaction with a heat and a particle reservoir

In addition to a heat bath, considering a particle reservoir is a common practice, especially in statistical physics. In the context of resource theories for quantum thermodynamics, such scenarios have been looked at in [35].

Systems in contact with both a heat and a particle reservoir, have equilibrium states

$$\rho = \sum_{E,N} \frac{e^{-\beta(E-N\mu)}}{\mathcal{Z}} \left|E,\ N\right\rangle \left\langle E,\ N\right| \tag{36}$$

in the eigenbasis $\{|E,\ N\rangle\}_{E,\ N}$, where E and N denote energy and particle number respectively and $\mathcal{Z}$ is the grand canonical partition function. Like in the case of a heat bath, we also include states for which only a subset of the eigenstates are populated as "equilibrium states". [14]

For quantum states ρ that are block diagonal in the energy-particle eigenbasis, the possibility of such processes can be expressed by an order relation $\prec_{\mathrm{N,T}}$, which consists again of a rescaling followed by majorization. Analogous to the Gibbs-rescaling, we can define a rescaled step function $f_\rho^{\mathrm{N,T}}$.

Definition 16. *Consider a block diagonal state in $\mathcal{S}(\mathcal{H})$:*

$$\rho = \sum_{\substack{E,N,n_{E,N},\\ n'_{E,N}}} \rho_{E,N,n_{E,N},n'_{E,N}} \left|E,N,n_{E,N}\right\rangle \left\langle E,N,n'_{E,N}\right| .$$

*Its spectrum can be denoted by a step function according to (12). Then, the **N,T-rescaled step function** of ρ is*

$$f_\rho^{\mathrm{N,T}}(x) = \begin{cases} \frac{p_i}{e^{-\beta(E_i-N_i\mu)}}, & \sum_{k=1}^{i-1} e^{-\beta(E_k-N_k\mu)} \le x \le \sum_{k=1}^{i} e^{-\beta(E_k-N_k\mu)}, \\ 0, & \textit{otherwise.} \end{cases}$$

For an equilibrium state ρ this is

$$f_\rho^{\mathrm{N,T}}(x) = \begin{cases} \frac{1}{\mathcal{Z}}, & 0 \le x \le \mathcal{Z}, \\ 0, & \text{otherwise,} \end{cases}$$

where $\mathcal{Z}$ is the grand canonical partition function of the occupied states.

Definition 17. *Let $\rho,\ \sigma \in \mathcal{S}(\mathcal{H})$ be two states which are block diagonal in the basis $\{|E,\ N\rangle\}_{E,\ N}$. The order of **N,T-majorization** $\prec_{\mathrm{N,T}}$ is defined as*

$$\rho \prec_{\mathrm{N,T}} \sigma \ \Leftrightarrow\ \int_0^k f_\rho^{\mathrm{N,T}}(x)dx \ge \int_0^k f_\sigma^{\mathrm{N,T}}(x)dx,\ \forall k \in \mathbb{R}_{\ge 0}.$$

This is analogous to Definition 10 but with an adapted rescaling operation. In analogy to Section IV, the operations corresponding to this order relation $\prec_{\mathrm{N,T}}$ are:

- composition with an ancillary systems in a state of the form (36);
- unitary transformation conserving the total energy and particle number of system and ancilla;
- removal of any subsystem.

For equilibrium states – which are always diagonal in the basis $\{|E,\ N\rangle\}_{E,\ N}$– this treatment suffices, whereas for those non-equilibrium states which contain coherent superpositions of such eigenstates it does not apply.

As for $\prec_{\mathrm{T}}$, the relation $\prec_{\mathrm{N,T}}$ fulfills Lieb and Yngvason's axioms. According to Theorem 1 there is thus a unique potential

$$S_{\mathrm{N,T}}(\rho) = \{\lambda : ((1-\lambda)\rho_0, \lambda\rho_1) \sim_{\mathrm{N,T}} \rho\}$$

for equilibrium states.

Proposition 18. *For an equilibrium state ρ the unique function $S_{\mathrm{N,T}}$ is*

$$S_{\mathrm{N,T}}(\rho) = a_{\mathrm{N,T}} \cdot \ln \mathcal{Z} + b_{\mathrm{N,T}}$$

with $a_{\mathrm{N,T}} > 0$.

Proof. Let $\rho \in \mathcal{S}(\mathcal{H})$ be an equilibrium state and let the equilibrium states $\rho_0 \prec\!\prec_{\mathrm{N,T}} \rho_1 \in \mathcal{S}(\mathcal{H})$ define a gauge. Then for $\lambda = S_{\mathrm{N,T}}(\rho)$, the relation $((1-\lambda)\rho_0, \lambda\rho_1) \sim_{N,T} \rho$ holds and is equivalent to

$$\int_0^k f^{\mathrm{N,T}}_{((1-\lambda)\rho_0,\lambda\rho_1)}(x)dx = \int_0^k f_\rho^{\mathrm{N,T}}(x)dx,\ \forall\ k \in \mathbb{R}_{\ge 0}.$$

As for equilibrium states $\rho \prec_{\mathrm{N,T}} \tilde\rho \Leftrightarrow \mathcal{Z}_{\tilde\rho} \ge \mathcal{Z}_\rho$ this is equivalent to

$$\mathcal{Z}_{\rho_0}^{1-\lambda}\mathcal{Z}_{\rho_1}^{\lambda} = \mathcal{Z}_\rho$$

and can be written as

$$\begin{aligned}\lambda &= \frac{1}{\ln \frac{\mathcal{Z}_{\rho_1}}{\mathcal{Z}_{\rho_0}}} \ln \mathcal{Z}_\rho - \frac{1}{\ln \frac{\mathcal{Z}_{\rho_1}}{\mathcal{Z}_{\rho_0}}} \ln \mathcal{Z}_{\rho_0} \\ &= a_{\mathrm{N,T}} \cdot \ln \mathcal{Z}_\rho + b_{\mathrm{N,T}},\end{aligned}$$

[14] For simplicity we assume that there are only particles of one kind.

where $a_{\rm N,T} = \frac{1}{\ln \frac{\mathcal{Z}_{\rho_1}}{\mathcal{Z}_{\rho_0}}}$ and $b_{\rm N,T} = -a_{\rm N,T} \cdot \ln \mathcal{Z}_{\rho_0}$. □

The "entropy function", i.e., the potential for a system in contact with a heat bath and a particle reservoir is related to the grand potential Ω, since

$$\Omega = -k_{\rm B} T \ln \mathcal{Z}.$$

For non-equilibrium states, the bounding functions $\tilde{S}_{\rm N,T-}$ and $\tilde{S}_{\rm N,T+}$ can be calculated analogously to the scenario including only a heat bath. They define bounds $\Omega_{\rm max}$ and $\Omega_{\rm min}$ on the potential Ω for non-equilibrium states. These are operationally related to the formation and destruction of a state in this scenario, again analogously to the case of a heat bath.

B. Interaction with an angular momentum reservoir

In the study of Landauer's principle [36], the question as to whether energy should obtain a special role among the conserved quantities or whether processes such as erasure could also be realized at an angular momentum instead of an energy cost was raised in Refs. [37, 38] and answered in the affirmative. We observe here that systems connected to an angular momentum reservoir can be included in the axiomatic framework.

As the consideration of an angular momentum reservoir is not common practice, we first sketch the concrete model of a spin reservoir from Refs. [37, 38]. The reservoir consists of N mobile spin-$\frac{1}{2}$ particles, for which the possible spin states are denoted by $|0\rangle$ and $|1\rangle$. The spin states are assumed to be degenerate in energy and thus decoupled from the spatial degrees of freedom, which are in equilibrium with a heat bath. The equilibrium probability for the reservoir to be in a particular state with n particles in state $|1\rangle$ and $N-n$ particles in state $|0\rangle$ is

$$p_{\rm n} = \frac{e^{-n\hbar\gamma}}{(1+e^{-\hbar\gamma})^N},$$

where the parameter γ is the analogue of the inverse temperature β encountered in the context of a heat bath. As for each value n there are $\binom{N}{n}$ such reservoir states, the normalization is given as $Z_{\rm J}^{\rm res} = (1+e^{-\hbar\gamma})^N$ and has the form of a partition function for the angular momentum reservoir. This construction allows us to consider an angular momentum reservoir of arbitrary size N. In the following, we consider a reservoir in the limit $N \to \infty$.

The state of a system in contact with a spin angular momentum reservoir can be described by a density operator. Again, we restrict our considerations to states that are block diagonal, this time in the eigenbasis of the z-component of the spin operator, denoted $\{|J\rangle\}_J$. To ensure that energy does not affect our considerations, we assume all spin-levels $|J\rangle$ to be energetically degenerate. A system in equilibrium with the reservoir is described by a density operator of the form

$$\rho = \sum_J \frac{e^{-J\hbar\gamma}}{Z_{\rm J}} |J\rangle\langle J| \tag{37}$$

with partition function $Z_{\rm J} = \sum_i e^{-J\hbar\gamma}$. (Note that we include states for which only a subset of the eigenstates are populated, as long as the projection onto the corresponding subspace has this form.) The spectra of block diagonal states can be represented in terms of rescaled step functions.

Definition 19. *Let*

$$\rho = \sum_{J,n_J,n'_J} \rho_{J,n_J,n'_J} |J,\ n_J\rangle\langle J,\ n'_J|$$

be a density matrix block diagonal in the eigenbasis of the z-component of the spin operator. Represent its spectrum according to (12)*. Then the* ***J-rescaled step function*** *of ρ is defined as*

$$f_\rho^J(x) = \begin{cases} \frac{p_i}{e^{-J(i)\hbar\gamma}}, & \sum_{k=1}^{i-1} e^{-J(k)\hbar\gamma} \le x \le \sum_{k=1}^{i} e^{-J(k)\hbar\gamma}, \\ 0, & \textit{otherwise.} \end{cases}$$

For an equilibrium state ρ this simplifies to

$$f_\rho^J(x) = \begin{cases} \frac{1}{Z_{\rm J}}, & 0 \le x \le Z_{\rm J}, \\ 0, & \text{otherwise.} \end{cases}$$

We describe the processes on a system in contact with an angular momentum reservoir as:

- composition with an ancillary system in an equilibrium state of the form (37);
- unitary transformation of system and ancilla conserving angular momentum;
- removal of any subsystem.

These lead to an ordering of the states by means of an order relation $\prec_{\mathrm{J}}$.

Definition 20. *Let ρ, $\sigma \in \mathcal{S}(\mathcal{H})$ be two states which are block diagonal in the basis $\{|J\rangle\}_J$. The relation of **J-majorization** $\prec_{\mathrm{J}}$ is defined as*

$$\rho \prec_{\mathrm{J}} \sigma \quad \Leftrightarrow \quad \int_0^k f_\rho^{\mathrm{J}}(x)dx \geq \int_0^k f_\sigma^{\mathrm{J}}(x)dx, \quad \forall k \in \mathbb{R}_{\geq 0}.$$

As in the case of a heat bath, the rescaled majorization relation $\prec_{\mathrm{J}}$ fulfills axioms E1 to E6 for equilibrium states and N1 and N2 for non-equilibrium states. This gives rise to a unique potential,

$$S_{\mathrm{J}} \propto \ln Z_{\mathrm{J}},$$

for equilibrium states. For non-equilibrium states, the two quantities $\tilde{S}_{\mathrm{J}-}$ and $\tilde{S}_{\mathrm{J}+}$ provide necessary conditions as well as a sufficient condition for state transformations under the above operations.

We have thus found an angular momentum based resource theory corresponding to the order relation $\prec_{\mathrm{J}}$, for which S_{J}, $\tilde{S}_{\mathrm{J}-}$ and $\tilde{S}_{\mathrm{J}+}$ are monotones. In agreement with [37, 38], energy can be substituted with angular momentum in our resource theoretic picture.

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