Thermodynamics of discrete quantum processes

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Abstract. We define thermodynamic configurations and identify two primitives of discrete quantum processes between configurations for which heat and work can be defined in a natural way. This allows us to uncover a general second law for any discrete trajectory that consists of a sequence of these primitives, linking both equilibrium and non-equilibrium configurations. Moreover, in the limit of a discrete trajectory that passes through an infinite number of configurations, i.e. in the reversible limit, we recover the saturation of the second law. Finally, we show that for a discrete Carnot cycle operating between four configurations one recovers Carnot's thermal efficiency.

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1. Introduction

The intuitive meaning of *heat* and *work* in thermodynamics is that of two types of energetic resources, one fully controllable and useful, the other uncontrolled and wasteful. An impressive effort has been devoted to provide a consistent mathematical characterization of these notions within a quantum mechanical description of physics [1–7]. This is a challenge since in contrast to other thermodynamic quantities, such as internal energy and entropy, heat and work are not properties of individual states of a system. They are defined for *continuous processes* connecting different states [2, 8, 9], implying that their statistical fluctuations cannot be described in terms of a single system observable. Two-point correlation functions characterizing the correlations along process paths are required—a problematic territory for quantum mechanics where definite trajectories cannot be fixed unless the system is continuously measured. Resolving these issues has been the topic of a number of publications that have formulated quantum trajectory approaches [2, 4, 6, 8–11].

In contrast here we focus on the *mean* values of heat and work where the analysis simplifies but still requires careful thought. We will adopt the identification of the system's internal energy with $U(\rho) = \text{tr}[\rho H]$ where ρ is the density matrix describing the state of the system at given time, and H is its instantaneous Hamiltonian. Clearly, a proper definition of this Hamiltonian is in general problematic. If the system is coupled to an environment the non-equilibrium behaviour of a general open system makes the definition of the system's Hamiltonian ambiguous [10, 12–15] both, mathematically and experimentally. Ultimately the choice of the Hamiltonian one assigns to the system must rely on the set of operations and observables one can access experimentally. In many situations of physical interest H can be

identified with the bare system Hamiltonian or an effective system Hamiltonian that incorporates the effect of the environment.

While the environment degrees are in principle uncontrolled, full control can be exerted over the temporal 'variation' of the system Hamiltonian. For instance, the size of a container in which steam is pumped can be freely chosen and a piston can be attached to the container that can push the wheels of a train. A formal definition of mean heat and work is then obtained by considering an infinitesimal change of the internal energy

$$dU = d\mathrm{tr}[\rho\, H] = \mathrm{tr}[\rho\, dH] + \mathrm{tr}[d\rho\, H], \tag{1}$$

associated with the time evolution of the system which brings its density matrix from ρ to $\rho + d\rho$ while the Hamiltonian varies from H to $H + dH$. The origin for the change of ρ may here be due to both, the variation of H induced by the experimenter and by the dynamics due to the coupling with the environment. The possibility of externally controlling H suggests to identify the first term on the rhs of equation (1) with the average work done by the experimenter during the evolution. The second term describes the internal energy change due to a reconfiguration of the system, i.e. a variation of the system's density matrix. This is an energy contribution over which the experimenter has no direct control and this is why it is associated with heat. The infinitesimal average *heat absorbed by the system* and the infinitesimal average *work done on the system* [12, 16–23] are therefore defined as

$$\delta Q := \mathrm{tr}[d\rho\, H] \quad \text{and} \quad \delta W := \mathrm{tr}[\rho\, dH], \tag{2}$$

with the symbol δ indicating that heat and work are in general no full differentials, i.e. they do not correspond to observables.

While the first law of thermodynamics states that the sum of the two average energy types is the average internal energy,

$$dU = \delta Q + \delta W, \tag{3}$$

the *split* into these two types of energies is crucial as it allows the formulation of the second law of thermodynamics. A fundamental law of physics, it sets limits on the work extraction of heat engines and establishes the notion of *irreversibility* in physics. The second law can be phrased in form of Clausius' inequality:

$$T\, dS \geqslant \delta Q, \tag{4}$$

stating that the change in a system's entropy must be larger than the average heat absorbed by the system during a process. While the first law of thermodynamics is fundamental for any process, the second law was originally stated for processes that *start and end in equilibrium*. Recently, the non-equilibrium work relation due to Jarzynski has been used to argue that the second law should also hold for any process starting from equilibrium, at temperature T, but ending in an arbitrary non-equilibrium state [24]. However, no conclusive argument has yet established the most general set of dynamical processes that obey the Clausius inequality [25].

Extending the infinitesimal scenario to *finite, continuous processes* in which the temporal evolution of $\rho(t)$ and $H(t)$ in time t is known, the mean heat and work can be found by integrating over the trajectory taken from $\rho(0)$ and $H(0)$ to $\rho(\tau)$ and $H(\tau)$, i.e.

$$Q := \int_0^\tau dt\, \mathrm{tr}[\dot{\rho}(t)\, H(t)], \tag{5}$$

$$W := \int_0^\tau dt\, \mathrm{tr}[\rho(t)\, \dot{H}(t)], \tag{6}$$

while the first law becomes

$$\Delta U := \int_0^\tau dt \, \frac{d}{dt} \text{tr}[\rho(t) \, H(t)] = Q + W. \tag{7}$$

The mathematical consistency of the above expressions and their compatibility with the predictions of thermodynamics have been verified for many models, for example, for processes that are induced by Markovian master equations [18].

There are two paradigmatic examples of *all work* and *all heat* processes that we introduce here and which will become important in the later part of the paper. The first process is a unitary process, which we will also refer to as *closed*, where the (non-equilibrium) evolution of the state is given by the Schrödinger equation,

$$\dot{\rho}(t) = -\frac{i}{\hbar} [H(t), \rho(t)]. \tag{8}$$

Mean heat and work are then

$$Q_{\text{unitary}} = -\frac{i}{\hbar} \int_0^\tau dt \, \text{tr}[[H(t), \rho(t)] \, H(t)] = 0, \tag{9}$$
$$W_{\text{unitary}} = \Delta U,$$

consistent with the physical intuition that *no* heat has been provided to the system during the evolution. The second example is a system that evolves through the action of a dissipative, i.e. *open*, Markov process via a master equation [26],

$$\dot{\rho}(t) = -\frac{i}{\hbar} [H, \rho(t)] + \mathcal{L}(\rho(t)), \tag{10}$$

with $\mathcal{L}$ being the dissipative Lindblad term. Under the assumption that the typical time scales associated with the time-independent H are much shorter than those associated with $\mathcal{L}$ we can treat the system as almost isolated and use equation (1) to compute its internal energy. In this limit equation (6) is valid with the Hamiltonian just being the time-independent H,

$$W_{\text{dissipative}} = 0, \tag{11}$$
$$Q_{\text{dissipative}} = \text{tr}[\rho(\tau) \, H] - \text{tr}[\rho(0) \, H] = \Delta U,$$

which is in full agreement with the physical intuition that no work has been performed on the system.

While these examples constitute special cases of continuous processes the heat and work in a general process depend intimately on the exact details of the process. However, the caveat with this viewpoint is that in most real life applications one does *not* know what the dynamics of the state of the system is nor what the appropriate local Hamiltonian is at all times. Importantly, this is not just due to our ignorance of what happens at the quantum level. Quantum physics has strong fundamental limitations on what we *can know* without choosing a measurement apparatus, measuring the system and interpreting the data. Moreover, if the system is indeed measured then the experimenter's choice of what degrees of freedom she actually measures will affect what the *measured* heat and work will be. In other words, we propose that there is no *one* average heat and work for a particular process, there are different sensible outcomes to this question and the answer depends on the choice of system Hamiltonians in time, $H(t)$, that corresponds to specific measurement choices.

The aim of this paper is to show that it is possible to formulate a general second law independently of these choices [27]. To achieve this we will depart entirely from the traditional

continuous trajectory approach and propose a rather drastic but pragmatic change of perspective. We develop a consistent framework of mean heat and work for *discrete thermodynamic processes*. The rationale for this approach is that while the true process is continuous, observations we make on the system are almost always discrete. (We will neglect here the possibility of monitoring through continuous weak measurements.) For discrete snapshots of the dynamics, we find that by decomposing the transition into possible sequences of two fundamental primitives, it is possible to define heat and work for the discrete process in a way that is experimentally and mathematically clear. This allows us to establish a general second law for discrete processes between equilibrium and non-equilibrium states and the analysis of a discrete Carnot cycle, where we uncover the usual Carnot efficiency [28–30].

The paper is structured as follows. In section 2 we review the traditional perspective on the second law and the definition of entropy. In section 3 we define the dynamical configuration space of a system that allows us to formulate a notion of two primitives for discrete processes in section 4, the discrete unitary transformations (DUTs) and the discrete thermalizing transformations (DTTs). Section 5 contains the main results of the paper. First we show that entropic inequalities when applied to discrete trajectories formed by concatenating DUTs and DTTs yields the second law of thermodynamics in the Clausius formulation. We then derive two consequences: we find the minimum and maximum heat for a single DUT and DTT sequence and prove the existence of a discrete trajectory, formed by sequences of DUTs and DTTs, that connects two given thermodynamical configurations while asymptotically saturating the Clausius inequality. Finally we identify a discrete trajectory that connects the same initial and final configurations as the continuous trajectory through a sequence of DUTs and DTTs, and which approximates the continuous heat. In section 6 we derive the thermal efficiency of a discrete cycle, the Carnot efficiency, and conclude in section 7.

2. Entropy and the second law

In 1865 Clausius established that the overall heat flow in any cyclic, reversible process vanishes, implying that the integral over any non-cyclic process must be path independent. This led him to define the state function *entropy*, S, and the entropy change, ΔS, between the final and initial point of a reversible process,

$$\oint_{\text{rev}} \frac{\delta Q}{T} = 0 \quad \Rightarrow \quad \int_{\text{rev}} \frac{\delta Q}{T} =: \Delta S. \tag{12}$$

Clausius also showed that any cyclic process, reversible or irreversible, obeys

$$\oint \frac{\delta Q}{T} \leqslant 0. \tag{13}$$

This relation is the basis for a formulation of the second law of thermodynamics, known as the *Clausius inequality*. It is a statement for all thermodynamic processes, not just cyclic ones, that start from equilibrium at temperature T,

$$\int \frac{\delta Q}{T} \leqslant \Delta S, \tag{14}$$

and it simplifies to $Q \leqslant T \Delta S$ when the system interacts with a bath at constant temperature, T. In this form Clausius' inequality establishes the existence of an upper bound to the heat received by the system.

Clearly, Clausius's goal was to characterize different forms of *energy* and their interconversion. However, by formulating the second law of thermodynamics he defined a new quantity: entropy. In contrast, in modern information theory the focus is on the *state* of a system. Entropy is here used as the central physical quantity to measure the amount of information of a state, while heat and work, and energy in general, have no well-defined purpose for the interpretation of information processing. This opens the possibility of turning Clausius' original argument around. It allows one to use the entropy change in discrete quantum processes to *define* the average heat and work. Before we proceed, let us first highlight that non-trivial entropy bounds exist for any process between two states.

A state ρ describes an amount of information, quantified by the *von Neumann entropy*, $S(\rho) = -\text{tr}[\rho \ln \rho]$. The evolution of a quantum system from an initial state ρ_i to a final state ρ_f through an arbitrary process, or *quantum channel*, has a meaningful associated entropy change,

$$\Delta S(\rho_i, \rho_f) = -\text{tr}[\rho_f \ln \rho_f] + \text{tr}[\rho_i \ln \rho_i], \tag{15}$$

which quantifies the change of the encoded amount of information. The entropy change is non-trivially bounded from above and below by virtue of the positivity of the *relative entropy* (classically Kullback–Leibler divergence [31]). The relative entropy, $S(\rho_1 \| \rho_2)$, between two states ρ_1 and ρ_2 characterizes the number of additional bits required to encode ρ_1 when using the diagonal basis of ρ_2, rather than the diagonal basis of ρ_1. It is defined as [32]

$$S(\rho_1 \| \rho_2) := \text{tr}[\rho_1 \ln \rho_1] - \text{tr}[\rho_1 \ln \rho_2], \tag{16}$$

and is a positive quantity

$$S(\rho_1 \| \rho_2) \geqslant 0 \quad \text{with equality iff} \quad \rho_1 = \rho_2. \tag{17}$$

Intuitively, the relative entropy is similar to a distance measure, however, it is important to keep in mind that it is asymmetric $S(\rho_1 \| \rho_2) \neq S(\rho_2 \| \rho_1)$. Rewriting the entropy change, equation (15), in two ways

$$\Delta S(\rho_i, \rho_f) = -\text{tr}[\Delta \rho \, \ln \rho_f] + S(\rho_i \| \rho_f) \tag{18}$$

$$= -\text{tr}[\Delta \rho \, \ln \rho_i] - S(\rho_f \| \rho_i), \tag{19}$$

a lower and upper bound on the entropy change emerge

$$-\text{tr}[\Delta \rho \, \ln \rho_i] \geqslant \Delta S(\rho_i, \rho_f) \geqslant -\text{tr}[\Delta \rho \, \ln \rho_f]. \tag{20}$$

From the information theory point of view, bounds on the entropy change are important in their own right as they characterize how much information is lost or gained.

If we now assume the special case that ρ_f is a thermal state for the Hamiltonian H_f at an inverse temperature β_f then the lower bound becomes

$$\Delta S(\rho_i, \rho_f) \geqslant \beta_f \, \text{tr}[\Delta \rho \, H_f]. \tag{21}$$

Interpreting $\text{tr}[\Delta \rho \, H_f]$ as the heat of the discrete process, the above expression would constitute the second law of thermodynamics. This is exactly what we will pursue in section 4, e.g. in equation (28).

Interestingly, from (20) it is apparent that also an upper bound on the entropy change exists that is rarely discussed in the literature. This maximum value of the entropy change is enforced to ensure that any reverse process, from ρ_f to ρ_i, also obeys the second law[3].

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[3] Indeed the upper bound can be cast in the form of the lower bound by simply reversing the role of the input and of the output configurations: i.e. $-\text{tr}[\Delta \rho \ln \rho_i] \geqslant \Delta S(\rho_i, \rho_f)$ becomes $\Delta S(\rho_f, \rho_i) \geqslant -\text{tr}[\Delta^{(R)} \rho \ln \rho_f]$, with $\Delta^{(R)} \rho = \rho_i - \rho_f = -\Delta \rho$ being the state increment for the reverse process.
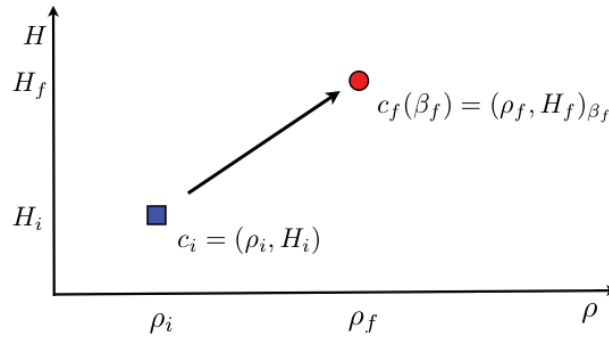
Figure 1. As a visual aid, points in dynamical configuration space are depicted in a (ρ, H)-coordinate system. A non-thermal configuration $c_i = (\rho_i, H_i)$ is shown as a blue square and a thermal configuration $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ is shown as a red circle. The discrete trajectory from c_i to $c_f(\beta_f)$ is indicated by the black arrow.

3. Dynamical configuration space

To assist our discussion of discrete quantum processes we introduce the concept of configuration space, following the spirit of [16, 17, 33], and propose a graphical representation for that space, see figure 1.

Definition 1. *Let S be the quantum system under investigation, with $\mathcal{H}_S$ its Hilbert space, $\mathcal{L}(\mathcal{H}_S)$ the set of linear operators on $\mathcal{H}_S$, and $\mathfrak{S}(\mathcal{H}_S) \subset \mathcal{L}(\mathcal{H}_S)$ the set of density matrices on $\mathcal{H}_S$. We define the dynamical configuration space $\mathcal{C}(\mathcal{H}_S)$ of S as the set formed by the pairs $(\rho, H) = c$ with $\rho \in \mathfrak{S}(\mathcal{H}_S)$ a density matrix[4] and $H \in \mathcal{L}(\mathcal{H}_S)$ a Hermitian operator on $\mathcal{H}_S$ whose spectrum is bounded from below. Points in the dynamical configuration space c are called 'configurations' to distinguish them from 'states', ρ.*

The evolution of the system is described by discrete trajectories in $\mathcal{C}(\mathcal{H}_S)$:

Definition 2. *A discrete trajectory $\mathcal{T}$ is defined as an ordered list of elements of $\mathcal{C}(\mathcal{H}_S)$ that describes the succession of configurations, with each element (ρ, H) containing both the density matrix ρ of S and the local Hamiltonian H of S at that specific instance of the evolution.*

We stress that both ρ and H of a configuration point $c \in \mathcal{C}(\mathcal{H}_S)$ have a clear experimental meaning. ρ is the density matrix that one would reconstruct by state tomography, i.e. the preparation of many copies of the same state ρ and the full tomographic measurement of its properties. The Hamiltonian of the system, H, is determined by the set of projective measurements $\{M_j\}_j$ the experimenter performs on the system to 'measure the energy' together with the interpretation of the corresponding energy eigenvalues, E_j, so that $H = \sum_j E_j M_j$. (The choice of the measurement and interpretation can be motivated by a process tomography on the Hamiltonian at any point in time. For this the system needs to be decoupled from the rest of the universe at that instance and evolve for a complete set of states for a short time interval τ through the action of H. By measuring the final states of the evolution the unitary $e^{-iH\tau}$ and hence H can be uncovered.) It is then straightforward to establish the internal energy and the entropy for each point in dynamical configuration space.

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[4] Density matrices are Hermitian and positive operators with normalized spectrum, $\text{tr}[\rho] = 1$.

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Definition 3. *For each configuration $c = (\rho, H)$ in $\mathcal{C}(\mathcal{H}_S)$ we define the internal energy as*

$$U(c) = \text{tr}[\rho H], \tag{22}$$

and the entropy as the von Neumann entropy $S(\rho)$ of ρ,

$$S(\rho) = -\text{tr}[\rho \ln \rho]. \tag{23}$$

A central notion in thermodynamics is the canonical Gibbs state, often also referred to as *thermal state* or *equilibrium* state. Since a thermal state, ρ, at temperature T is well-defined only with respect to a certain Hamiltonian, H, it is actually the *configuration $c = (\rho, H)$* that is thermal.

Definition 4. *An element $(\rho, H) \in \mathcal{C}(\mathcal{H}_S)$ describes a thermal equilibrium configuration (or briefly thermal configuration) if ρ is a Gibbs state of the Hamiltonian, H, for some finite inverse temperature $\beta > 0$, i.e.*

$$\rho = \frac{e^{-\beta H}}{Z(\beta)}, \tag{24}$$

with $Z(\beta) = \text{tr}[e^{-\beta H}]$ being the associated partition function[5]. In the following the thermal configurations will be indicated by $c(\beta) := (\rho, H)_\beta$ with the subscript β specifying the configuration's temperature.

Thermal configurations $(\rho, H)_\beta$ are very special. Firstly, for a given Hamiltonian, H, from all possible states that have a fixed value of the internal mean energy, $U = \text{tr}[\rho H]$, the thermal state maximizes the entropy $S(\rho) = -\text{tr}[\rho \ln \rho]$. In other words $c(\beta) = (\rho, H)_\beta$ is the most unbiased configuration one can assert to the system given only the knowledge of U [34]. Another insightful characterization of thermal configurations in terms of a property called *complete passivity* was achieved by Lenard [17], building on ideas of Pusz and Woronowicz [16]. Complete passivity captures the intuitive notion of thermal equilibrium. A configuration (ρ, H) is said to be *passive* if no work can be extracted from the system, i.e. $W \geqslant 0$ cf equation (6), when subjected to any unitary transformation for a time τ generated by an arbitrary time-dependent Hamiltonian with the sole constraint that $H(\tau) = H(0) = H$. A configuration $c = (\rho, H)$ is *completely passive* if all its regularized configurations $c^{(n)} := (\rho^{\otimes n}, H^{(n)} = \sum_{j=1}^{n} H_j)$ are passive for $n = 1, 2, \ldots$. Here the unitary operations entering in this definition are generated by *arbitrary* time-dependent Hamiltonians $H^{(n)}(t)$ that satisfy the constraint $H^{(n)}(0) = H^{(n)}(\tau) = H^{(n)}$. That is during $t \in]0, \tau[$, $H^{(n)}(t)$ is allowed to introduce any sort of interactions between the various copies of ρ. It turns out that while all $c = (\rho, H)$ with commuting ρ and H are passive configurations, only thermal configurations $c(\beta)$ and the ground state are *completely passive* [16, 17]. To stress the special role of thermal configurations graphically, they are denoted as red circles while all configuration that are not thermal will be called *non-equilibrium* configurations and are depicted as blue squares, see figure 1.

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[5] Note, that in the definition we have explicitly assumed β to be finite. In the zero temperature limit the associated density matrix ρ of the thermal configuration $c(\beta \to \infty)$ approaches the projector on the ground state of H. The limiting case does however not belong to the set of the thermal configurations but to their closure. This definition ensures that the density matrices ρ of the thermal configurations $c(\beta)$ are always full rank and hence strictly positive, i.e. the state has no zero eigenvalue.

A note on gauge.   Given a generic state $\rho \in \mathfrak{S}(\mathcal{H}_S)$ which is full rank, there always exists a Hermitian operator $H \in \mathcal{L}(\mathcal{H}_S)$ and a $\beta > 0$ such that $(\rho, H)_\beta$ is thermal[6] at the inverse temperature β. In fact the problem admits infinite solutions, since there are two gauge freedoms for the choice of H and β. Firstly, the zero-point of the energy scale can be chosen arbitrarily by a constant a. The second gauge, b, is the temperature itself, which sets a spacing of the energy scale. The pair $\{H, \beta\}$ is equivalent to $\{b(H + a), \beta/b\}$ in that they have the same set of thermal configurations. In particular the internal energy (22) and the entropy (23) of such configurations do not depend on the values of a and b. In the following we will assume that both gauges have been chosen to some fixed values.

4. Discrete transformations in dynamical configuration space

Among all possible discrete transformations in dynamical configuration space $\mathcal{C}(\mathcal{H}_S)$ we identify two classes that admit a clear analysis of the energetic balance and can be used as primitives for general discrete dynamical evolutions.

4.1. Discrete unitary transformations (DUTs)

These transformations map an initial configuration $c_i = (\rho_i, H_i)$ to a final configuration $c_f = (\rho_f, H_f)$, denoted as $c_i \xrightarrow{\text{DUT}} c_f$, with the only constraint that

$$\rho_f = V\rho_i V^\dagger, \tag{25}$$

for some *unitary V*. No constraint is posed on the relationship between H_i and H_f. The definition of DUTs is inspired by continuous unitary transformations, see equation (8). There the system is thermally isolated while evolving through the action of some external force that modifies the Hamiltonian in time, $H(t)$, and generates arbitrary unitary evolutions $V = \mathcal{T}e^{-i\int_0^\tau dt\, H(t)/\hbar}$ where $\mathcal{T}$ indicates time ordering. For the discrete mapping $c_i \xrightarrow{\text{DUT}} c_f$ no assumption is made on the time duration τ nor the specific form of $H(t)$ which realizes the unitary V. In analogy to the continuous situation, we define the work done on the system due to a DUT identical to the total variation of the internal energy, ΔU, i.e.

$$W\left(c_i \xrightarrow{\text{DUT}} c_f\right) := U(c_f) - U(c_i) = \text{tr}[\rho_i\,(V^\dagger H_f V - H_i)], \tag{26}$$

while no heat is associated with DUTs, i.e.

$$Q\left(c_i \xrightarrow{\text{DUT}} c_f\right) := 0. \tag{27}$$

    A special class of DUTs are the *discrete unitary quenches* (DUQs). Experimentally, a quench is an abrupt, instantaneous change of the system Hamiltonian which leaves the system density matrix unchanged, i.e. $V = \mathbb{1}$, $(\rho_i, H_i) \xrightarrow{\text{DUQ}} (\rho_i, H_f)$. We also note that for full rank states ρ_i a DUQ can be found that brings (ρ_i, H_i) to a final configuration that is thermal, $c_f(\beta) = (\rho_i, \tilde{H}_f)_\beta$, with the Hamiltonian defined as $\tilde{H}_f = -\frac{1}{\beta}(\ln \rho_i + \ln Z)$.

    DUTs will be denoted as blue arrows in the graphical representation of the configuration space, see figure 2. These 'work arrows' indicate the closed nature of the transformation.

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[6] When ρ is not full rank there is no thermal configuration $c(\beta)$ whose density matrix exactly coincides with ρ. However, it is still possible to find Gibbs configurations whose density matrices are arbitrarily close to ρ.
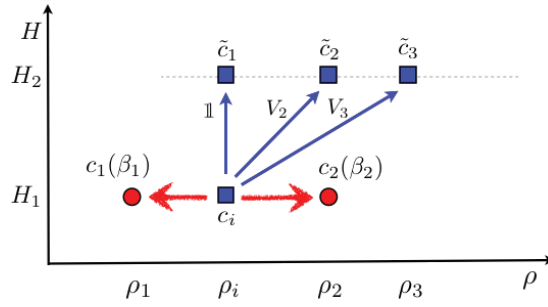
Figure 2. Originating from the initial state $c_i = (\rho_i, H_1)$ three DUTs are shown, depicted as blue arrows, each ending at a final configuration $\tilde{c}_j = (\rho_j = V_j \, \rho_i \, V_j^\dagger, H_2)$ for $j = 1, 2, 3$. The special case where c_i is transformed into $\tilde{c}_1$ is an example of a DUQ. Also shown are two DTTs, depicted as red fuzzy arrows, originating from c_i and ending at thermal configurations $c_1(\beta_1) = (\rho_1, H_1)_{\beta_1}$ and $c_2(\beta_2) = (\rho_2, H_1)_{\beta_3}$ where β_1 and β_2 are inverse temperatures associated with the thermal configurations.

The DUTs characteristic properties are summarized here:

1. DUTs can start from and end at either non-thermal or thermal configurations.
2. DUTs change the state by a unitary and no entropy change is induced by a DUT, i.e.
   $\Delta S(c_i \stackrel{\text{DUT}}{\to} c_f) = S(\rho_f) - S(\rho_i) = 0$.
3. DUTs can be concatenated to produce another DUT.
4. Any DUT has an inverse that is also a DUT.

4.2. Discrete thermalizing transformations (DTTs)

DTTs are defined as those transformations which take a generic $c_i = (\rho_i, H)$ into a Gibbs state at some inverse temperature β, $c_f(\beta) = (\rho_1 = \frac{e^{-\beta H}}{Z}, H)_\beta$, without modifying the system Hamiltonian H. The prototypical example of a DTT is an arbitrary thermalization process in which the system is put into a weak thermal contact with a reservoir at inverse temperature β and left until its state becomes time-independent. Physically this is realized by the system weakly interacting with a large external environment. The requirement of a *small* coupling ensures a clear definition of a local system Hamiltonian. For example, the dissipative evolution $(\rho(t), H)$ defined in equation (10) with the additional assumption that the Lindblad term $\mathcal{L}$ commutes with H will for $t \to \infty$ converge to ρ_1. In analogy with this continuous process, we assume that the internal energy change due to a DTT is a result solely of the heat absorbed by the system

$$Q(c_i \stackrel{\text{DTT}}{\to} c_f(\beta)) := U(c_f(\beta)) - U(c_i) = \text{tr}[H(\rho_f - \rho_i)], \tag{28}$$

while the work of a DTT vanishes,

$$W(c_i \stackrel{\text{DTT}}{\to} c_f(\beta)) := 0. \tag{29}$$

This non-trivial expression of the heat is exactly of the form that we expected from the bounds on the entropy in equation (21), and it will be the basis for deriving a general second law for discrete quantum trajectories in the next section.

DTTs will be denoted as horizontal red arrows in the graphical representation, see figure 2. The fuzziness of these 'heat arrows' indicates the open nature of the transformation. The characteristic properties of DTTs are summarized here:

1. DTTs always end in thermal configurations.
2. DTTs do not change the Hamiltonian.
3. The entropy change associated with a DTT is in general non-zero, i.e. $\Delta S(c_i \overset{\text{DTT}}{\to} c_f(\beta)) = S(\rho_f) - S(\rho_i) \neq 0$
4. DTTs can be concatenated to produce another DTT.
5. The inverse of a DTTs is in general not a DTT. Only if the initial configuration c_i was already thermal, can the action of a DTT be reversed by another DTT. The lack of an inverse is a direct consequence of the inherently irreversible nature of this transformation.

5. Heat and Clausius inequality for discrete thermodynamic processes

Having identified two fundamental process primitives in configuration space, we now focus on more complex discrete trajectories. These can start from equilibrium or non-equilibrium configurations, however, we restrict ourselves to discrete trajectories that can be obtained by concatenating DUT and DTTs. Within this scenario we will be able to formulate a general second law for discrete quantum processes, that does not require detailed knowledge of the continuous state and local Hamiltonian evolution.

5.1. Single DUT + DTT transformations

Let us begin with the simplest non-trivial discrete transformation which can be used to connect two equilibrium configurations.

5.1.1. Equilibrium to equilibrium processes. We consider a trajectory that starts from a thermal configuration $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i}$ and ends at a final thermal configuration $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ via the action of a single DUT followed by a DTT. The heat of the discrete process can then be determined as the sum of the heats of each component, for both of which the heat is a well-defined quantity. The DUT first unitarily rotates the input density matrix to $\rho_1 = V \rho_i V^\dagger$ while the Hamiltonian changes from H_i to H_f, ending in an intermediate (not necessarily thermal) configuration $c_1 = (\rho_1, H_f)$. A DTT follows that brings c_1 to $c_f(\beta_f)$, resulting in the discrete overall trajectory

$$c_i(\beta_i) \overset{\text{DUT}}{\longrightarrow} c_1 \overset{\text{DTT}}{\longrightarrow} c_f(\beta_f), \tag{30}$$
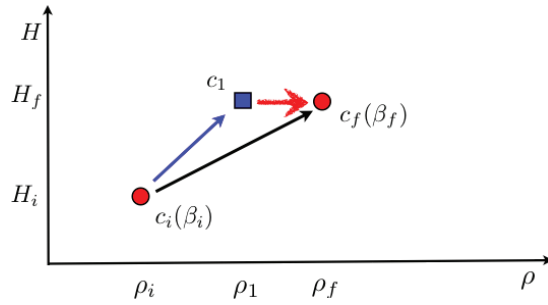
shown in figure 3.

While heat of process (30) is only exchanged during the DTT, the amount of exchanged heat depends on the DUTs unitary V

$$Q(c_1 \overset{\text{DTT}}{\to} c_f(\beta_f)) = \text{tr}[(\rho_f - V \rho_i V^\dagger) H_f]. \tag{31}$$

Clearly, the value of the heat depends on the choice of the unitary V with the maximum and minimum heat given by

$$Q_{\max} = \sum_{k=1}^{N} H_f(k) \left(\frac{e^{-\beta_f H_f(k)}}{Z_f} - \frac{e^{-\beta_i H_i(k)}}{Z_i} \right), \tag{32}$$

Figure 3. Trajectory connecting two Gibbs configurations, $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i} \to c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ (black arrow) and discrete decomposition into a DUT, $c_i(\beta_i) \to c_1$ (blue arrow), to an intermediate point $c_1 = (\rho_1, H_f)$ followed by a DTT, $c_1 \to c_f(\beta_f)$ (red arrow).

$$Q_{\min} = \sum_{k=1}^{N} H_f(k) \left(\frac{e^{-\beta_f H_f(k)}}{Z_f} - \frac{e^{-\beta_i H_i(N-k+1)}}{Z_i} \right), \tag{33}$$

where $\{H_f(k)\}_k$ and $\{H_i(k)\}_k$ are the eigenvalues of H_f and H_i ordered in decreasing order and $Z_{i,f}$ the partition functions of the initial and final configuration. The derivation of this expression and the corresponding unitaries $V_{\min}$ and $V_{\max}$, are given in appendix A.

However, for any possible choice of the DUT connecting $c_i(\beta_i)$ to the intermediate step c_1, i.e. for any unitary transformation V, a second law can be established by linking the heat and the entropy change. The entropy change is bounded according to equation (20), by

$$\begin{aligned} \Delta S(\rho_i, \rho_f) &= S(\rho_f) - S(\rho_1) \\ &\geqslant -\operatorname{tr}[(\rho_f - \rho_1) \ln \rho_f] = \beta_f \operatorname{tr}[(\rho_f - V\rho_i V^\dagger) H_f], \end{aligned} \tag{34}$$

implying

$$\Delta S(\rho_i, \rho_f) \geqslant \beta_f \, Q(c_i \to c_f). \tag{35}$$

Thus the process (30) obeys a Clausius-type inequality, see (14), which states that the heat absorbed by the system is upper bounded by the entropy change.

5.1.2. Non-equilibrium to non-equilibrium processes. We now turn to discrete non-equilibrium processes for which establishing the Clausius inequality in the continuous case has only recently been addressed [25]. In our approach this can be done by observing that given two generic configurations $c_i = (\rho_i, H_i)$ and $c_f = (\rho_f, H_f)$ in $\mathcal{C}(\mathcal{H}_S)$, it is always possible to connect them via a discrete trajectory composed by three primitive steps which differs from the one given in equation (30) only by a final DUQ transformation[7]. Specifically we can write

$$\mathcal{T} := c_i \xrightarrow{\text{DUT}} c_1 \xrightarrow{\text{DTT}} c_2(\beta_2) \xrightarrow{\text{DUQ}} c_f, \tag{36}$$

with intermediate configurations $c_1 = (V\rho_i V^\dagger, H_1)$ and $c_2(\beta_2) = (\rho_f, H_1)_{\beta_2}$. The first and the last step of (36) do not alter the entropy of the system, nor contribute to the heat exchange since

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[7] Alternative discrete trajectories connecting c_i and c_f can be considered; by choosing as the last step of this sequence a DUQ transformation—a special case of a DUT—the energy analysis simplifies to a minimum.
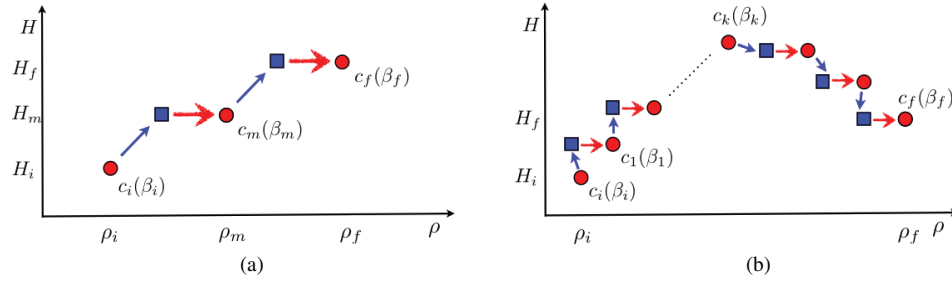
Figure 4. Panel (a) shows the realization of a general transformation $c_i(\beta_i) \to c_f(\beta_f)$ as a sequence of two DUT + DTT transformations, via an intermediate thermal configuration, $c_m(\beta_m) = (\rho_m, H_m)_{\beta_m}$. Panel (b) shows the realization of a general transformation $c_i(\beta_i) \to c_f(\beta_f)$ through a sequence of DUT + DTT transformations, via many intermediate thermal configurations, $c_k(\beta_k) = (\rho_k, H_k)_{\beta_k}$.

they are DUTs. This implies the identity $\Delta S(\rho_i, \rho_f) = \Delta S(\rho_1, \rho_2)$ and allows us to identify the heat associated with $\mathcal{T}$ with the quantity

$$Q(\mathcal{T}) = Q(c_1 \xrightarrow{\text{DTT}} c_2(\beta_2)) = \text{tr}[(\rho_f - V\rho_i V^\dagger)H_1]. \tag{37}$$

The lower bound of equation (20) can then be used to establish a Clausius-type inequality for the discrete transformation (36), i.e.

$$\Delta S(\rho_i, \rho_f) \geqslant -\text{tr}[(\rho_f - V\rho_i V^\dagger) \ln \rho_f] = \beta_2 \, Q(\mathcal{T}), \tag{38}$$

where β_2 is the temperature of the intermediate configuration $c_2(\beta_2)$. Returning now to the relationship between heat and entropy discussed in section 2 we interpret the above inequality as giving an upper bound to the thermodynamic quantity, $\beta_2 Q(\mathcal{T})$, evaluated along the trajectory $\mathcal{T}$. Different trajectories will have different values of $Q(\mathcal{T})$—for some trajectories the right hand side may even vanish—but for all trajectories the thermodynamic quantity on the right hand side is non-trivially bounded from above by the entropy change. While the Clausius inequality remains the same, the role of heat and entropy has been inverted at the conceptual level. Here entropy change is the *more fundamental* quantity than heat, which has to be characterized for each possible discrete trajectory.

5.2. Sequences of DUT + DTTs

The trajectories defined in equations (30) and (36) are just specific choices of discrete trajectories connecting two configurations c_i and c_f. We will now show that a Clausius inequality, e.g. inequalities of the type (35), holds for general discrete processes as long as they can be decomposed as a *sequence* of DUT + DTTs steps. To show this, we first consider the discrete trajectory, γ, pictured in panel (a) of figure 4 where $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i}$ is transformed into $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ via two DUT + DTT transformations and a third thermal configuration $c_m(\beta_m) = (\rho_m, H_m)_{\beta_m}$, i.e.

$$\gamma := c_i(\beta_i) \xrightarrow{\text{DUT+DTT}} c_m(\beta_m) \xrightarrow{\text{DUT+DTT}} c_f(\beta_f). \tag{39}$$

In this scenario the following inequality for the entropy holds:

$$\Delta S(\rho_i, \rho_f) = \Delta S(\rho_i, \rho_m) + \Delta S(\rho_m, \rho_f) \geqslant \beta_m \, Q_m + \beta_f \, Q_f, \tag{40}$$

where $Q_m = Q(c_i(\beta_i) \xrightarrow{\text{DUT+DTT}} c_m(\beta_m))$ and $Q_f = Q(c_m(\beta_m) \xrightarrow{\text{DUT+DTT}} c_f(\beta_f))$, and where equation (35) was used for the two DUT + DTT transformations.

Inequality (40) can immediately be generalized to an arbitrary number of intermediate DUT + DTT steps connecting $c_i(\beta_i)$ to $c_f(\beta_f)$. Specifically, consider a generic discrete trajectory $\mathcal{T}$ composed of N consecutive DUT + DTT steps that pass through the thermal configurations $\{c_i(\beta_i), c_1(\beta_1), c_2(\beta_2), \ldots, c_{N-1}(\beta_{N-1}), c_f(\beta_f)\}$ as shown in panel (b) in figure 4. Then by expressing the total entropy increment $\Delta S(\rho_i, \rho_f)$ as a sum of terms $\Delta S(\rho_k, \rho_{k+1})$ associated with the various steps of $\mathcal{T}$ and applying equation (35) to each one of them, the Clausius inequality becomes

$$\Delta S(\rho_i, \rho_f) \geqslant \sum_{k=0}^{N-1} \beta_{k+1} \, Q(c_k(\beta_k) \xrightarrow{\text{DUT+DTT}} c_{k+1}(\beta_{k+1})). \tag{41}$$

The generality of this derivation implies that sequences of discrete unitary and DTTs always fulfil a Clausius-type equation.

To formulate this as a lemma, we introduce a useful discrete process quantity, Λ, for a DUT + DTT sequence,

$$\Lambda(c_k(\beta_k) \xrightarrow{\text{DUT+DTT}} c_{k+1}(\beta_{k+1})) := \beta_{k+1} \text{tr}[(\rho_{k+1} - V_k \, \rho_k \, V_k^\dagger) \, H_{k+1}],$$
$$= \beta_{k+1} \, Q(c_k(\beta_k) \xrightarrow{\text{DUT+DTT}} c_{k+1}(\beta_{k+1})). \tag{42}$$

The quantity Λ is the discrete analogue to the continuous expression $\int \frac{\delta Q}{T}$. For the trajectory $\mathcal{T}$ the overall $\Lambda(\mathcal{T})$ is obtained by summing over the Λ contributions of the various steps, i.e.

$$\Lambda(\mathcal{T}) := \sum_{k=0}^{N-1} \Lambda(c_k(\beta_k) \xrightarrow{\text{DUT+DTT}} c_{k+1}(\beta_{k+1})), \tag{43}$$

with $k = 0$ and N corresponding to the initial and final configurations, i and f, respectively[8]. From equation (41) then follows:

Lemma 1. *Any trajectory $\mathcal{T}$ made of sequences of DUT+DTTs fulfils a Clausius inequality of the form*

$$\Delta S(\rho_i, \rho_f) \geqslant \Lambda(\mathcal{T}). \tag{44}$$

While in general a single DUT + DTT process cannot saturate the equality, see appendix A, we will now show that augmenting intermediate steps will always increase the rhs of equation (41). Moreover, we find that in the limit of infinitely long sequences the asymptotic saturation of the inequality (41) is always possible.

5.3. Saturating the Clausius bound

To show that the entropy bound equation (41) can be saturated we construct a class of trajectories $\mathcal{T}'$ from a generic DUT + DTT trajectory $\mathcal{T}$, as depicted in panel (b) of figure 4, for which the functional $\Lambda(\mathcal{T}')$ is always larger than $\Lambda(\mathcal{T})$. One class of trajectories $\mathcal{T}'$ is the trajectory identical to $\mathcal{T}$ however with the step $\tilde{c}_k \xrightarrow{\text{DTT}} c_{k+1}(\beta_{k+1})$ replaced with the sequence

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[8] Note, that while this definition of Λ requires the initial and final configurations to be thermal, it is possible to generalize this definition to non-thermal configurations by including additional initial and final transformations in a similar way to the trajectory in equation (36).
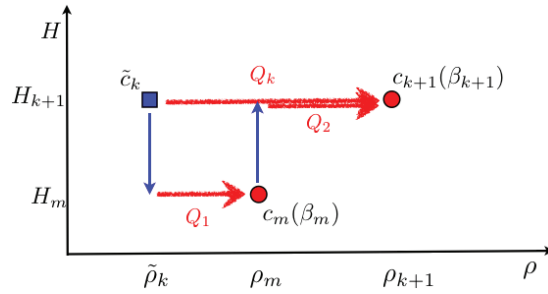
Figure 5. Discrete trajectory connecting $\tilde{c}_k \to c_{k+1}(\beta_{k+1})$ by a single DTT with heat Q_k, and by a sequence of two DUQ+DTT transformations via an intermediate thermal configurations, $c_m(\beta_m) = (\rho_m, H_m)_{\beta_m}$. The two DTTs have heats Q_1 and Q_2, respectively.

$\tilde{c}_k \xrightarrow{\text{DUQ+DTT}} c_m(\beta_m) \xrightarrow{\text{DUQ+DTT}} c_{k+1}(\beta_{k+1})$ as shown in figure 5, where $c_m(\beta_m) = (\rho_m, H_m)_{\beta_m}$ has an intermediate density matrix

$$\rho_m = p\,\tilde{\rho}_k + (1-p)\,\rho_{k+1}, \tag{45}$$

with mixing probability $p \in]0, 1[$.[9] The increment on the rhs of (44) for the new trajectory $\mathcal{T}'$, $\Delta(\mathcal{T}', \mathcal{T}) = \Lambda(\mathcal{T}') - \Lambda(\mathcal{T}) = \beta_m Q_1 + \beta_{k+1} Q_2 - \beta_{k+1} Q_k$, see figure 5, is then *strictly positive* for any p

$$\Delta(\mathcal{T}', \mathcal{T}) = -\text{tr}[\ln \rho_m\,(\rho_m - \tilde{\rho}_k)] - \text{tr}[\ln \rho_{k+1}\,(\rho_{k+1} - \rho_m)] + \text{tr}[\ln \rho_{k+1}\,(\rho_{k+1} - \tilde{\rho}_k)]$$
$$> -pS(\tilde{\rho}_k\|\tilde{\rho}_k) - (1-p)\,S(\rho_{k+1}\|\tilde{\rho}_k) - pS(\rho_{k+1}\|\tilde{\rho}_k) \tag{46}$$

$$- (1-p)\,S(\rho_{k+1}\|\rho_{k+1}) + S(\rho_{k+1}\|\tilde{\rho}_k)$$
$$= 0, \tag{47}$$

where we have assumed $\tilde{\rho}_k \neq \rho_{k+1}$, and used equation (45) and the joint convexity of the relative entropy [32],

$$S(\rho_1\|p\tilde{\rho}_k + (1-p)\rho_{k+1}) \leqslant pS(\rho_1\|\tilde{\rho}_k) + (1-p)S(\rho_1\|\rho_{k+1}), \tag{48}$$

$$S(p\tilde{\rho}_k + (1-p)\rho_{k+1}\|\rho_1) \leqslant pS(\tilde{\rho}_k\|\rho_1) + (1-p)S(\rho_{k+1}\|\rho_1) \tag{49}$$

with equality *iff* $\rho_{k+1} = \rho_1 = \tilde{\rho}_k$. We summarize this result in the following lemma:

Lemma 2. *Adding intermediate thermal configurations $c_m(\beta_m)$ (see equation (45)) to any trajectory $\mathcal{T}$ results in a new trajectory $\mathcal{T}'$ with increased Λ, i.e.*

$$\Delta(\mathcal{T}', \mathcal{T}) = \Lambda(\mathcal{T}') - \Lambda(\mathcal{T}) > 0. \tag{50}$$

Having confirmed that it is possible for any given discrete trajectory to introduce intermediate steps such that the rhs of equation (44) increases, the task is now to show that the entropy bounds can be saturated by reiterating the procedure. The proof relies on lower

[9] $c_m(\beta_m)$ is a well-defined thermal configuration as its state is by construction full rank.

bounding Λ and showing that the bound converges to the upper bound on Λ, equation (44), in the limit of infinite steps. The detailed derivation is given in appendix B proving the following theorem:

Theorem 1. *Let $\mathcal{T}$ be a discrete trajectory connecting the initial Gibbs configuration $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i}$ to the final Gibbs configuration $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ via a sequence of N concatenated $\mathrm{DUT} + \mathrm{DTT}$ steps $c_k(\beta_k) \overset{\mathrm{DUT+DTT}}{\longrightarrow} c_{k+1}(\beta_{k+1})$ connecting the thermal configurations $\mathcal{T} = \{c_i(\beta_i) = c_0(\beta_0), c_1(\beta_1), \ldots, c_N(\beta_N) = c_f(\beta_f)\}$ as in panel (b) in figure 4. Then a sequence of trajectories $\mathcal{T}'_n$ exists, obtained from $\mathcal{T}$ by adding n intermediate thermal steps, which saturates the Clausius bound (41) in the asymptotic limit, i.e.*

$$\Delta S(\rho_i, \rho_f) = \lim_{n \to \infty} \Lambda(\mathcal{T}'_n). \tag{51}$$

5.4. Approximation of continuous processes by discrete processes

In the introduction we have seen that for continuous processes where consistent definitions of $\rho(t)$ and of the local Hamiltonian $H(t)$ can be assigned for all t, equation (5) defines the heat absorbed by the system. We have already discussed the difficulties of knowing $\rho(t)$ and identifying a proper local Hamiltonian $H(t)$ for the system. However, in what follows we will assume that some 'valid' continuous trajectory $c(t) = (\rho(t), H(t)) \in \mathcal{C}(\mathcal{H}_s)$ is given for which equations (5) and (6) apply. We now wish to identify a discrete trajectory that connects the same initial and final configurations as the continuous trajectory through a sequence of DUTs and DTTs, and which approximates the continuous heat. The analysis leads to the following theorem:

Theorem 2. *For a continuous process between two configurations c_0 and c_τ that obeys the Clausius inequality, a discrete trajectory Γ' exists that connects the same configurations and has exactly the same heat as the continuous process.*

Proof. Consider an infinitesimal heat increment along the continuous trajectory,

$$\delta Q(t) = \mathrm{tr}[(\rho(t) - \rho(t - dt))H(t)], \tag{52}$$

with $\rho(t)$ and $\rho(t - dt)$ being the density matrices of two infinitesimally separated configurations on the trajectory. Define the initial and final configuration for a discrete trajectory to be $c_i = (\rho(t - dt), H(t - dt)) =: (\rho_1, H_i)$ and $c_f = (\rho(t), H(t)) := (\rho_2, \tilde{H}_2)$. To compare the continuous heat (52) with a discrete heat we need to identify a discrete trajectory, γ, connecting the same initial and final configuration as the continuous trajectory.

One example is the sequence γ shown as a solid line in figure 6,

$$\gamma := c_i \overset{\mathrm{DUQ}}{\to} c_1 \overset{\mathrm{DTT}}{\to} \tilde{c}_2(1) \overset{\mathrm{DUQ}}{\to} \hat{c}_2 \overset{\mathrm{DTT}}{\to} c_2(1) \overset{\mathrm{DUQ}}{\to} c_f, \tag{53}$$

where $\tilde{c}_2(1) = (\tilde{\rho}_2, \tilde{H}_2)_{\beta=1}$ and $c_2(1) = (\rho_2, H_2)_{\beta=1}$ are equilibrium configurations[10] and $\hat{c}_2 = (\tilde{\rho}_2, H_2)$ is a non-equilibrium configuration. The inverse temperatures of the equilibrium configurations $\tilde{c}_2(1)$ and $c_2(1)$ are both chosen $\beta = 1$. Heat Q_i,

$$Q_i := Q(c_i \overset{\mathrm{DUQ+DTT}}{\longrightarrow} \tilde{c}_2(1)) = Q(c_1 \overset{\mathrm{DTT}}{\longrightarrow} \tilde{c}_2(1)) = -\mathrm{tr}[(\tilde{\rho}_2 - \rho_1) \ln \tilde{\rho}_2], \tag{54}$$

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[10] A proper definition of $c_2(1)$ requires ρ_f to be full rank. If this is not the case one can still define a trajectory (53) with c_f replaced by a full rank configuration which can be chosen to be arbitrarily close to c_f.
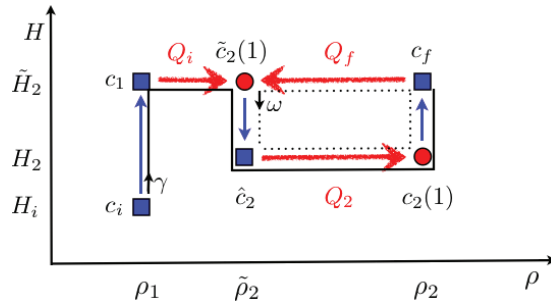
Figure 6. The figure shows the initial and final non-equilibrium configurations, c_i and c_f, of the continuous process. A discrete trajectory, γ, that connects c_i and c_f is also indicated (solid). Also shown is the closed loop discrete trajectory ω (dotted). The two thermal configurations $\tilde{c}_2(1) = (\tilde{\rho}_2, \tilde{H}_2)_{\beta=1}$ and $c_2(1) = (\rho_2, H_2)_{\beta=1}$ are both chosen with inverse temperature $\beta = 1$, as indicated in the circles.

is exchanged when passing from $c_0 \to \tilde{c}_2(1)$ via a DUQ+DTT through the intermediate configuration c_1, see figure 6. Heat Q_2,

$$Q_2 := Q(\hat{c}_2 \xrightarrow{\text{DTT}} c_2(1)) = -\text{tr}[(\rho_2 - \tilde{\rho}_2)\ln\rho_2], \tag{55}$$

is exchanged when passing from $\hat{c}_2 \to c_2(1)$. Therefore

$$Q(\gamma) = Q_i + Q_2. \tag{56}$$

On the other hand, the continuous heat increment $\delta Q(t)$ can be decomposed into two heat contributions,

$$\delta Q(t) = \text{tr}[(\rho(t) - \rho(t - dt))H(t)] = \text{tr}[(\rho_2 - \rho_1)\tilde{H}_2] \tag{57}$$

$$= \text{tr}[(\rho_2 - \tilde{\rho}_2)\tilde{H}_2] + \text{tr}[(\tilde{\rho}_2 - \rho_1)\tilde{H}_2] \tag{58}$$

$$= -\text{tr}[(\rho_2 - \tilde{\rho}_2)\ln\tilde{\rho}_2] - \text{tr}[(\tilde{\rho}_2 - \rho_1)\ln\tilde{\rho}_2] \tag{59}$$

$$= -Q_f + Q_i. \tag{60}$$

where Q_f would be the heat absorbed by the system if it passed from c_f to $\tilde{c}_2(1)$ via a DTT, i.e.

$$Q_f := Q(c_f \xrightarrow{\text{DTT}} \tilde{c}_2(1)) = -\text{tr}[(\tilde{\rho}_2 - \rho_2)\ln\tilde{\rho}_2]. \tag{61}$$

To compare the continuous heat (57) with the discrete heat (56), we introduce a second discrete trajectory ω. This is a closed loop sequence of DUQ and DTT transformations, see figure 6,

$$\omega := \tilde{c}_2(1) \xrightarrow{\text{DUQ}} \hat{c}_2 \xrightarrow{\text{DTT}} c_2(1) \xrightarrow{\text{DUQ}} c_f \xrightarrow{\text{DTT}} \tilde{c}_2(1). \tag{62}$$

In trajectory ω heat is exchanged from $\hat{c}_2 \to c_2(1)$ and from $c_f \to \tilde{c}_2(1)$, so $Q(\omega) = Q_2 + Q_f$. As discussed in previous sections the discrete heat always obeys the Clausius inequality (35), and with $\beta = 1$ for both steps this implies

$$0 = \Delta S(\tilde{\rho}_2, \tilde{\rho}_2) \geqslant Q_2 + Q_f \tag{63}$$
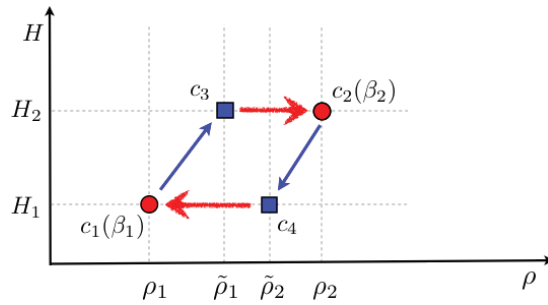
Figure 7. Representation of the cycle of equation (66).

for trajectory ω. Using this in equation (56) we find that the heat associated with the discrete trajectory γ from c_i to c_f is a *lower bound* to the infinitesimal continuous heat for the same initial and final configuration, (52), i.e.

$$Q(\gamma) = Q_i + Q_2 \leqslant Q_i - Q_f = \delta Q(t). \tag{64}$$

This can immediately be extended to the full continuous process: for any arbitrary continuous process between c_0 and c_τ there is always a discrete trajectory Γ between the same two configurations that has a lower heat than the continuous heat, equation (5). Moreover, by augmenting intermediate steps in the discrete trajectory Γ, resulting in the trajectory Γ' that passes through an infinite sequence of points $c(t)$, it is possible to increase the associated heat, as shown in section 5.2. From theorem 1 follows that if the continuous trajectory fulfils the Clausius inequality, then a discrete trajectory connecting the same initial and final configuration can be found that has the same heat as the continuous trajectory. $\qquad\square$

Theorem 2 opens a number of interesting questions. While it implies that a Clausius-obeying continuous trajectory can be simulated in terms of a sequence of DUT and DTTs, it is left open if *all* continuous trajectories can be approximated by discrete trajectories. Secondly, the theorem establishes the existence of an approximating infinite sequence but it remains open if a *finite* sequence can be found that connects the same configurations and has exactly the same heat as the continuous process. Thirdly, one would expect the infinite discrete sequence to *converge* to the continuous trajectory. To establish the relationship between these two trajectories in future work it will be necessary to identify a metric in configuration space from which a notion of convergence can be derived.

6. Thermal efficiency

The last piece in our analysis of the energy balance in discrete quantum processes is to determine the efficiency of a discrete cyclic process, such as the one depicted in figure 7 where $c_1(\beta_1) = (\rho_1, H_1)_{\beta_1}$, $c_2(\beta_2) = (\rho_2, H_2)_{\beta_2}$ are equilibrium configurations, while $c_3 = (\tilde{\rho}_1, H_2)$, and $c_4 = (\tilde{\rho}_2, H_1)$ are not. This results in the following lemma:

Lemma 3. *The thermal efficiency of the discrete cycle depicted in figure 7 is bounded by the Carnot efficiency,*

$$\eta \leqslant 1 - \frac{T_1}{T_2}, \tag{65}$$

and the optimal efficiency is achievable.

Proof. For the overall loop,

$$c_1(\beta_1) \overset{\text{DUT}}{\to} c_3 \overset{\text{DTT}}{\to} c_2(\beta_2) \overset{\text{DUT}}{\to} c_4 \overset{\text{DTT}}{\to} c_1(\beta_1), \tag{66}$$

the entropy change is zero. However, the entropy change nevertheless bounds the heat of the two heat-producing DTT processes, $c_3 \to c_2(\beta_2)$ and $c_4 \to c_1(\beta_1)$,

$$\Delta S = 0 \geqslant \beta_2 \, Q(c_3 \to c_2) + \beta_1 \, Q(c_4 \to c_1). \tag{67}$$

This implies that at least one of the two heats must be negative. Let us assume for instance that the heat exchanged with the thermal reservoir at temperature $T_2 = 1/(k_B \beta_2)$ is positive, $Q(c_3 \to c_2) > 0$, while the other heat is negative $Q(c_4 \to c_1) < 0$ (other scenarios can be treated analogously, see below). The total heat absorbed per cycle is

$$Q(c_1 \to c_1) = Q(c_3 \to c_2) + Q(c_4 \to c_1), \tag{68}$$

with the energy balance implying that the overall absorbed heat must be equal to the negative work done on the system during the cycle,

$$0 = \Delta U(c_1 \to c_1) = Q(c_1 \to c_1) + W(c_1 \to c_1). \tag{69}$$

The thermal efficiency is defined as the ratio between the work performed and the heat absorbed, leading to

$$\eta = \frac{-W(c_1 \to c_1)}{Q(c_3 \to c_2)} = \frac{Q(c_1 \to c_1)}{Q(c_3 \to c_2)} = \frac{Q(c_3 \to c_2) + Q(c_4 \to c_1)}{Q(c_3 \to c_2)} \tag{70}$$

$$\leqslant 1 - \frac{\beta_2}{\beta_1} = 1 - \frac{T_1}{T_2}, \tag{71}$$

where we used equation (67). If $T_1 \leqslant T_2$ the system absorbs heat from a higher temperature bath and gives heat to a lower temperature bath. The efficiency η is then positive and smaller than unity with the optimal efficiency reproducing the classical Carnot efficiency [28–30]. The optimal efficiency can be reached by augmenting the discrete trajectory to saturate the equality in the Clausius inequality, see theorem 1. □

Remark. If instead $T_2 \geqslant T_1$, i.e. heat is absorbed from a lower temperature bath and given to one at a higher temperature, the system operates as a refrigerator. In this case the total work *absorbed* by the system, $W(c_1 \to c_1) = Q(c_3 \to c_2)(T_1/T_2 - 1)$, is positive. The efficiency of the process can be measured by the coefficient of performance, $\text{COP}_{\text{cooling}}$, defined as the ratio between the heat absorbed from the cold reservoir T_2 (i.e. $Q(c_3 \to c_2)$) and the total work done on the system

$$\text{COP}_{\text{cooling}} = \frac{Q(c_3 \to c_2)}{W(c_1 \to c_1)} \leqslant \frac{T_2}{T_1 - T_2}, \tag{72}$$

which again is always smaller than one. Finally, if the signs for the heats $Q(c_3 \to c_2)$ and $Q(c_4 \to c_1)$ are interchanged the above argument still holds with equations (70) and (72) being replaced by the inequalities $\eta \leqslant 1 - \frac{T_2}{T_1}$ and $\text{COP}_{\text{cooling}} \leqslant \frac{T_1}{T_2 - T_1}$, respectively.

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7. Conclusions

The early development of thermodynamics culminating in the formulation of the second law also gave birth to a new quantity, the entropy, whose physical meaning was at first opaque. Only later was its meaning elucidated by the works of Boltzmann and others. In this paper we proposed to turn the original argument around and use the well-established notion of entropy that characterizes the information content in a (quantum) state to motivate the definition of a notion of heat for discrete quantum processes. The approach circumvents the large cluster of problems surrounding the idea of a unique definition of heat and work in processes where (i) the Hamiltonian of the system is not well-defined due to the open nature of the system and (ii) there are fundamental limitations on the notion of trajectories where full knowledge is only given at discrete points in time when a measurement with a specific Hamiltonian occurred.

By introducing thermodynamic configurations, identifying two primitives for discrete processes, DUTs and DTTs, and defining heat to pertain only to DTTs we were able to uncover a general second law valid for any discrete process consisting of sequences of DUT + DTTs between both, equilibrium and non-equilibrium configurations. Moreover, we showed that an infinite sequence of DUT + DTT processes exists that saturates the Clausius inequality. In other words, saturation occurs when a discrete trajectory is mapped out into a continuous one by a sequence of measurements that are infinitely close together. This provides a link between *reversibility*—here the reversibility—of a discrete process—and the equality in the second law for discrete processes, reminiscent of the Clausius' statement of equality for thermodynamic reversible continuous processes, equation (12). On the other hand, we also showed that for any continuous process between two configurations that obeys the Clausius inequality, there exists a discrete process between the same configurations with the same heat. Finally, we showed that for the discrete version of a thermodynamic cycle, formed by a discrete trajectory passing through four configurations Carnot's efficiency is recovered.

The strength of our approach is to give meaning to heat and work, reversibility and efficiency following from just a few sensible and simple definitions. In some respect this is analogous to the axiomatic approach to thermodynamics first developed by Carathéodory [35]. We hope that the presented analysis will inspire discussions and future work on characterizing heat and work in quantum processes. Of course many open questions remain. One direction of particular relevance is clearly the identification of a proper *metric* in configuration space, that would allow to quantify, in a precise and (hopefully) operationally well defined way, how distant two generic discrete trajectories are.
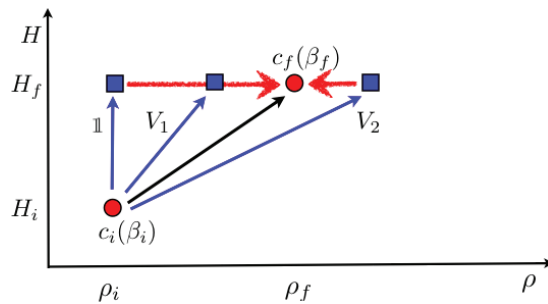
Appendix A. Minimum and maximum heat for a single DUT + DTT process

Here we discuss the impact of the unitary V of equation (31) on the heat of the DUT + DTT process (30). Specifically, we want to identify the DUTs that maximize and minimize the heat

Figure A.1. Realizations of the map from the Gibbs state $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i}$ to the Gibbs state $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$ via some DUT, specified by a unitary V, followed by an appropriate DTT.

on the rhs of equation (35) and establish if a DUT exists that leads to a saturated Clausius equality. The last question can be easily solved by noticing that saturation occurs only when the inequality holds in equation (34). However, this is only true iff $\rho_1 = \rho_f$, i.e. ρ_i and ρ_f must be unitarily equivalent for some unitary V_0, $V_0 \rho_i V_0^\dagger = \rho_f$. In other words equivalence in (30) requires that no DTT enters in the process so that $\Delta S(\rho_i, \rho_f) = 0$. For any non-trivial DTT a finite gap between the lhs and the rhs of equation (35) exists. (This is not true however for sequences of DUT–DTT transformations as considered in section 5.3.)

To determine the minimum/maximum gap we require the maximum/minimum heat with respect to all possible DUTs of a DUT + DTT process connecting two thermal configurations $c_i(\beta_i) = (\rho_i, H_i)_{\beta_i}$ and $c_f(\beta_f) = (\rho_f, H_f)_{\beta_f}$, see figure A.1, i.e.

$$Q_{\max} := \max_V \mathrm{tr}[(\rho_f - V \rho_i V^\dagger) H_f], \tag{A.1}$$

$$Q_{\min} := \min_V \mathrm{tr}[(\rho_f - V \rho_i V^\dagger) H_f], \tag{A.2}$$

where the maximization/minimization is taken over all unitary transformations V. This task is solved with the following lemma.

Lemma 4. *Given $A = \sum_j \alpha_j |\alpha_j\rangle\langle\alpha_j|$ and $B = \sum_j \beta_j |\beta_j\rangle\langle\beta_j|$ Hermitian operators on a finite dimensional Hilbert space $\mathcal{H}$, with α_j and β_j being their corresponding eigenvalues which are ordered in decreasing order (i.e. $\alpha_j \geqslant \alpha_{j+1}$, $\beta_j \geqslant \beta_{j+1}$). Then the minimum of $\mathrm{tr}[A V B V^\dagger]$ over the set of unitary transformations is achieved by the unitary $V_{\min}$ which maps the eigenvector $\{|\beta_j\rangle\}$ of B into the eigenvectors $\{|\alpha_j\rangle\}$ of A in such a way that*

$$V_{\min}|\beta_j\rangle = |\alpha_{N-j+1}\rangle, \tag{A.3}$$

i.e. the maximum eigenvector of B is mapped into the minimum eigenvector of A. As a consequence the minimum expectation value is

$$\min_V \mathrm{tr}[A V B V^\dagger] = \mathrm{tr}[A V_{\min} B V_{\min}^\dagger] = \sum_j \alpha_j \beta_{N-j+1}. \tag{A.4}$$

Similarly the maximum of $\mathrm{tr}[A V B V^\dagger]$ over the set of unitary transformations is achieved by the unitary $V_{\max}$ that maps the eigenvectors $\{|\beta_j\rangle\}$ of B into the eigenvectors $\{|\alpha_j\rangle\}$ of A in such

a way that

$$V_{\max}|\beta_j\rangle = |\alpha_j\rangle. \tag{A.5}$$

Consequently the maximum expectation value is

$$\max_V \mathrm{tr}[A\ V\ B\ V^\dagger] = \mathrm{tr}[A\ V_{\max}\ B\ V_{\max}^\dagger] = \sum_j \alpha_j\beta_j. \tag{A.6}$$

Proof. These minimum and maximum expectation values are a trivial consequence of the theorem 2 of [17]. □

Application of equations (A.4) and (A.6) gives the minimum and maximum heat for the DUT + DTT process (30)

$$Q_{\max} = \sum_{k=1}^N H_{\mathrm{f}}(k) \left(\frac{\mathrm{e}^{-\beta_{\mathrm{f}} H_{\mathrm{f}}(k)}}{Z_{\mathrm{f}}} - \frac{\mathrm{e}^{-\beta_{\mathrm{i}} H_{\mathrm{i}}(k)}}{Z_{\mathrm{i}}} \right), \tag{A.7}$$

$$Q_{\min} = \sum_{k=1}^N H_{\mathrm{f}}(k) \left(\frac{\mathrm{e}^{-\beta_{\mathrm{f}} H_{\mathrm{f}}(k)}}{Z_{\mathrm{f}}} - \frac{\mathrm{e}^{-\beta_{\mathrm{i}} H_{\mathrm{i}}(N-k+1)}}{Z_{\mathrm{i}}} \right), \tag{A.8}$$

where $\{H_{\mathrm{f}}(k)\}_k$ and $\{H_{\mathrm{i}}(k)\}_k$ are the eigenvalues of H_{f} and H_{i} ordered in decreasing order.

Appendix B. Proof of theorem 1

Consider the kth step of the trajectory $\mathcal{T}$ in panel (b) in figure 4, which connects the thermal points $c_k(\beta_k) = (\rho_k, H_k)_{\beta_k}$ and $c_{k+1}(\beta_{k+1}) = (\rho_{k+1}, H_{k+1})_{\beta_{k+1}}$. We define a new trajectory $\mathcal{T}'_{k;n}$ which is identical with the original trajectory $\mathcal{T}$ except that the kth step is now replaced with a sequence of $n-1$ intermediate *thermal configurations* $c'_1(1), \ldots, c'_{n-1}(1)$ that are linked through a DUQ–DTT sequence

$$c_k \xrightarrow{\mathrm{DUQ+DTT}} c'_1 \quad \cdots \quad \xrightarrow{\mathrm{DUQ+DTT}} c'_{n-1} \xrightarrow{\mathrm{DUQ+DTT}} c_{k+1}. \tag{B.1}$$

The configurations $c'_\ell(1)$ have density matrices $\rho'_1, \ldots, \rho'_{n-1}$ defined by the mixtures

$$\rho'_\ell = \left(1 - \frac{\ell}{n} \right) \rho_k + \frac{\ell}{n} \rho_{k+1} \quad \text{for} \quad \ell = 0, \ldots, n, \tag{B.2}$$

where $\rho'_0 = \rho_k$ and $\rho'_n = \rho_{k+1}$. Applying the Clausius inequality (41) in the form of (44) to sequence (B.1) yields

$$\Delta S(\rho_k, \rho_{k+1}) \geqslant \Lambda(\mathcal{T}'_{k;n}). \tag{B.3}$$

By definition (42), the transformations being *discrete unitaries* and the fact that intermediate inverse temperatures are all set to 1, $\Lambda(\mathcal{T}'_{k;n})$ can be expressed as

$$\Lambda(\mathcal{T}'_{k;n}) = \sum_{\ell=0}^{n-1} \mathrm{tr}[(\rho'_\ell - \rho'_{\ell+1})\ \ln \rho'_{\ell+1}] = \mathrm{tr}\left[(\rho_k - \rho_{k+1}) \frac{1}{n} \sum_{\ell=0}^{n-1} \ln \rho'_{\ell+1} \right]. \tag{B.4}$$

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On the other hand the entropy change $\Delta S(\rho_k, \rho_{k+1})$ can be lower bounded by

$$\Delta S(\rho_k, \rho_{k+1}) = \sum_{\ell=0}^{n-1} \Delta S(\rho'_\ell, \rho'_{\ell+1}) \tag{B.5}$$

$$\leqslant \sum_{\ell=0}^{n-1} \text{tr}[(\rho'_\ell - \rho'_{\ell+1}) \ln \rho'_\ell] = \text{tr}\left[(\rho_k - \rho_{k+1}) \frac{1}{n} \sum_{\ell=0}^{n-1} \ln \rho'_\ell\right] \tag{B.6}$$

$$= \Lambda(\mathcal{T}'_{k;n}) + \text{tr}\left[(\rho_k - \rho_{k+1}) \frac{\ln \rho_k - \ln \rho_{k+1}}{n}\right] \tag{B.7}$$

$$= \Lambda(\mathcal{T}'_{k;n}) + \frac{S(\rho_{k+1}\|\rho_k) + S(\rho_k\|\rho_{k+1})}{n}, \tag{B.8}$$

which implies

$$\Lambda(\mathcal{T}'_{k;n}) \geqslant \Delta S(\rho_k, \rho_{k+1}) - \frac{S(\rho_{k+1}\|\rho_k) + S(\rho_k\|\rho_{k+1})}{n}. \tag{B.9}$$

ρ_k and ρ_{k+1} are density matrices of Gibbs configurations and thus of full rank. Consequently, the quantity $S(\rho_{k+1}\|\rho_k) + S(\rho_k \| \rho_{k+1})$ is finite[11]. From equations (B.3) and (B.9) it then follows that $\Lambda(\mathcal{T}'_{k;n})$ converges to $\Delta S(\rho_k, \rho_{k+1})$ for $n \to \infty$, i.e.

$$\Delta S(\rho_k, \rho_{k+1}) = \lim_{n \to \infty} \Lambda(\mathcal{T}'_{k;n}). \tag{B.10}$$

In other words by augmenting the intermediate points of which connects $c_k(\beta_k)$ and $c_{k+1}(\beta_{k+1})$ we can saturate the associated Clausius inequality for the kth step of the trajectory $\mathcal{T}$. By repeating the same procedure for each of the steps of $\mathcal{T}$ a new trajectory emerges as the union of the individual sequences

$$\mathcal{T}'_n = \bigcup_{k=1}^{N-1} \mathcal{T}'_{k;n_k}, \tag{B.11}$$

where n is the multidimensional variable $(n_1, n_2, \ldots, n_{N-1})$. Lemma 1 follows from the additivity of Λ (43) and taking the limit of each $n_k \to \infty$ (B.10). $\qquad \square$

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