

NEW DEFINITIONS OF THERMODYNAMIC TEMPERATURE AND ENTROPY NOT BASED ON THE CONCEPTS OF HEAT AND THERMAL RESERVOIR

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ABSTRACT. From a new rigorous formulation of the general axiomatic foundations of thermodynamics we derive an operational definition of entropy that responds to the emergent need in many technological frameworks to understand and deploy thermodynamic entropy well beyond the traditional realm of equilibrium states of macroscopic systems. The new treatment starts from a previously developed set of carefully worded operational definitions for all the necessary basic concepts, and is not based on the traditional ones of “heat” and of “thermal reservoir”. It is achieved in three steps. First, a new definition of thermodynamic temperature is stated, for any stable equilibrium state. Then, by employing this definition, a measurement procedure is developed which defines uniquely the property entropy in a broad domain of states, which could include *in principle* even some non-equilibrium states of few-particle systems, provided they are separable and uncorrelated. Finally, the domain of validity of the definition is extended, possibly to every state of every system, by a different procedure, based on the preceding one, which associates a range of entropy values to any state not included in the previous domain. The principle of entropy non-decrease and the additivity of entropy are proved in both the domains considered.

1. Introduction

Thermodynamic entropy plays a crucial role in the development of the physical foundations of a variety of emerging technologies — nanomaterials, small-scale hydrodynamics, chemical kinetics for energy and environmental engineering and biotechnologies, electrochemistry, quantum entanglement in quantum information, non-equilibrium bulk and interface phenomena, etc. — which require a clear understanding of the meaning and role of thermodynamic entropy beyond the traditional equilibrium and macroscopic realms, well into the non-equilibrium and few-particle domains currently being explored very actively in many fields of science and technology (see, e.g., Verley and Lacoste (2012), Brandão *et al.* (2013), Horodecki and Oppenheim (2013), and Skrzypczyk *et al.* (2014) for recent attempts to extend thermodynamics to nonequilibrium states and individual quantum systems). In traditional treatments of thermodynamics (see, e.g. Fermi (1956), Pippard (1957), and Zemansky (1968)), the definitions of thermodynamic temperature and of entropy are based

on the concepts of *heat* and of *thermal reservoir*. Usually, heat is not defined rigorously. For instance, in his lectures on physics, Feynman *et al.* (1963) describe heat as one of several different forms of energy related to the jiggling motion of particles; in this picture, heat appears as a transfer of kinetic energy and the difference between heat and work is not clarified. Landau (1980) defines heat as the part of an energy change of a body that is not due to work done on it. However, there are interactions between systems which are neither heat nor work, such as, for instance, exchanges of radiation between systems in nonequilibrium states. Guggenheim (1967) defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan (1941) defines heat as the energy transferred from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. These definitions do not describe clearly the phenomena which occur at the interface between the interacting systems; moreover, they require a previous definition of *empirical temperature*, a concept which, in turn, is usually not defined rigorously. Another drawback of the employment of heat in the definition of entropy is the following: since heat, when properly defined, requires the existence of subsystems in stable equilibrium at the boundary between the interacting systems, a definition of entropy based on heat can hold, at most, in the domain of *local equilibrium* states.

An alternative method for the axiomatization of thermodynamics was developed at MIT by Hatsopoulos and Keenan (1965) and by Gyftopoulos and Beretta (2005). The main progress obtained in these references, with respect to the traditional treatments, is a more general definition of entropy — not based on the heuristic notions of empirical temperature and heat, and not restricted *a priori* to stable equilibrium states — that emerges from a complete set of operational definitions of the basic concepts, such as those of system, property, state, and stable equilibrium state, and a new statement of the second law expressed as a postulate of existence, for a system with fixed composition and constraints, of a unique stable equilibrium state for each value of the energy.

Improvements of this method, yielding more rigorous definitions of isolated system, environment of a system and external force field, as well as a more direct definition of entropy, have been proposed over the years by Zanchini (1986, 1988, 1992), Zanchini and Beretta (2008, 2010), Beretta and Zanchini (2011), and Zanchini and Beretta (2014). Such constructions are important because they provide rigorous operational definitions of entropy potentially valid also in the non-equilibrium domain. However, they still require the use of a thermal reservoir as an auxiliary system (that plays the role of an *entropy meter*) in the operational procedure that defines how to measure the entropy difference between any two states of a system. As already pointed out by Gyftopoulos and Beretta (2005, p.87), such use of thermal reservoirs has both logical and operational drawbacks.

A thermal reservoir, when properly defined (Gyftopoulos and Beretta 2005; Zanchini and Beretta 2010; Beretta and Zanchini 2011), is a closed system R , contained in a fixed region of space, such that whenever R is in stable equilibrium it is also in mutual stable equilibrium with a duplicate of itself, kept in any of its stable equilibrium states. Once thermodynamic temperature has been defined, it turns out that a thermal reservoir has the same temperature in all its stable equilibrium states, independently of the value of the energy.

This condition is fulfilled by the simple-system model¹ of a pure substance kept in the range of triple-point stable equilibrium states, because within such range of states energy can be added or removed at constant volume without changing the temperature. Hence, pure substances in their triple-point ranges are good practical examples of thermal reservoirs that can be easily set up in any laboratory.

However, the triple-point model is only an approximate description of reality, valid with exceedingly good approximation for systems with many particles of the order of one mole, but not in general, *e.g.*, not for systems with few particles. In a fully explicit axiomatic treatment one could declare the existence of thermal reservoirs as an assumption, but then one could prove that, strictly, thermal reservoirs cannot exist. Thus, from the strictly logical point of view, the use of the thermal reservoir in the definition of entropy is an internal inconsistency.

Another important drawback of the use of a thermal reservoir R in the measurement procedure that defines the entropy difference of two states A_1 and A_2 of a system A is that the procedure (see Gyftopoulos and Beretta (2005), Zanchini and Beretta (2010), Beretta and Zanchini (2011), and Zanchini and Beretta (2014)) requires to measure the energy change of the reservoir R in a reversible weight process for the composite system AR in which A changes from state A_1 to state A_2 . If system A has only few particles, then the energy change of R will be extremely small and hardly detectable if, as just discussed, the thermal reservoir R can only be realized by means of a macroscopic system.

The scope of the present paper is to develop new general definitions of thermodynamic temperature and thermodynamic entropy that are neither based on the concept of heat nor on that of thermal reservoir, so that both the logical and the practical drawbacks due to the use of these concepts are removed.

A procedure which yields the definitions of temperature and entropy without employing the concepts of heat and of thermal reservoir was presented by Carathéodory (1909). However, his treatment is valid only for stable equilibrium states of simple systems in the sense established by Gyftopoulos and Beretta (2005, Ch.17). The same restriction holds for some developments of Carathéodory's method (see Turner (1960), Landsberg (1961), Sears (1963), and Giles (1964)), aimed at making the treatment simpler and less abstract.

Another axiomatization of thermodynamics has been developed in recent years by Lieb and Yngvason (1999, 2013, 2014). Their method is based on establishing an order relation between states, denoted by the symbol \prec , through the concept of adiabatic accessibility: a state Y is said to be adiabatically accessible from a state X , *i.e.*, $X \prec Y$, if it is possible to change the state from X to Y by means of an adiabatic process. By introducing a suitable set of Axioms concerning the order relation \prec , the authors prove the existence and the *essential uniqueness* (Lieb and Yngvason 1999) of entropy. While the treatment presented by Lieb and Yngvason (1999) holds only for stable equilibrium states of simple systems or collections of simple systems, through the complements presented by Lieb and Yngvason (2013, 2014) the validity is extended respectively to non-equilibrium states by Lieb and Yngvason (2013) and, through the use of a simple system as an *entropy meter*, also to non-simple systems (Lieb and Yngvason 2014). Since to exhibit simple-system behavior

¹As defined and discussed by Gyftopoulos and Beretta (2005, pp.263-265), the simple-system model is appropriate for macroscopic systems with many particles, but fails for few-particle systems for which, *e.g.*, rarefaction effects near walls cannot be neglected.

the entropy meter must be a many-particle system, when applied to few-particle systems the definition could present the same kind of ‘practical’ problems faced by our previous definitions based on the entropy meter being a thermal reservoir.

In the present paper, a set of postulates and assumptions analogous to that stated by Zanchini and Beretta (2014) is employed, but here the definitions of thermodynamic temperature and thermodynamic entropy are obtained *without employing the concept of thermal reservoir*. The main result of the new formulation is that by avoiding to use as entropy meter a many-particle system, we derive a rigorous and general operational definition of thermodynamic entropy which holds, potentially, also for some non-equilibrium states of non-simple and non-macroscopic systems. Then, the domain of validity of the definition is extended to include possibly every state of every system by a procedure, similar to that developed by Lieb and Yngvason (2013), which associates a range of entropy values to any state not included in the previous domain.

The potential applicability to non-equilibrium states is a relevant feature in the framework of the fast growing field of non-equilibrium thermodynamics (see, e.g., Kjelstrup and Bedeaux (2008)), where research advances seem to substantiate from many perspectives the validity of a general principle of maximum entropy production (Gheorghiu-Svirschevski 2001a,b; Martyushev and Seleznev 2006; Beretta 2009, 2014). It is also relevant in the framework of the recently growing field of thermodynamics in the quantum regime, where much discussion about the microscopic foundations of thermodynamics is still taking place (see, e.g., Maddox (1985), Beretta (1986), Bennett (2008), Hatsopoulos and Beretta (2008), Lloyd (2008), Maccone (2009), Beretta (2012), Verley and Lacoste (2012), Brandão *et al.* (2013), Horodecki and Oppenheim (2013), Skrzypczyk *et al.* (2014), Brandão *et al.* (2015), Cano-Andrade *et al.* (2015), and Weilenmann *et al.* (2016)).

The definition of entropy presented here is complementary to that developed by Lieb and Yngvason: indeed, while Lieb and Yngvason (1999, 2013, 2014) focused their demonstrations on the proof of existence and essential uniqueness of an entropy function which is additive and fulfils the principle of entropy nondecrease, the present treatment identifies a general measurement procedure suitable to determine the entropy values. The principle of entropy nondecrease and the additivity of entropy are then proved as consequences of the definition.

In order to focus immediately on the construction of the new general definition of entropy, we keep to a minimum the discussion of the preliminary concepts. Instead, we provide in footnotes full proofs of the lemmas, theorems, and corollaries.

2. Summary of basic preliminary definitions

In this section, we very briefly summarize the definitions of terms and preliminary concepts that we will use in the rest of the paper. A complete set of operational definitions of these concepts is available in (Zanchini and Beretta 2010; Beretta and Zanchini 2011).

System. With the term *system* we mean a set of material particles, of one or more kinds, such that, at each instant of time, the particles of each kind are contained within a given region of space. Regions of space containing different kinds of particles can overlap and even coincide. If the external boundary surface of the union of the regions of space which contain the particles of the systems is a *wall*, *i.e.*, a surface that cannot be crossed by material

particles, the system is called *closed*.

Property. Any system is endowed with a set of reproducible measurement procedures; each procedure that involves a single instant of time defines a *property* of the system.

State. The set of all the values of the properties of a system, at a given instant of time, defines the *state* of the system at that instant.

External force field. A system can be in contact with other matter, or surrounded by empty space; moreover, force fields due to external matter can act in the region of space occupied by the system. If, at an instant of time, all the particles of the system are removed from the respective regions of space and brought far away, but a force field is still present in the region of space (previously) occupied by the system, then this force field is called an *external force field*. An external force field can be either gravitational, or electric or magnetic, or a superposition of the three.

Environment of a system. Consider the union of all the regions of space spanned by a system during its entire time evolution. If no other material particles, except those of the system, are present in the region of space spanned by the system or touches the boundary of this region, and if the external force field in this region is either vanishing or stationary, then we say that the system is *isolated*. Suppose that an isolated system I can be divided into two subsystems, A and B . Then, we can say that B is the *environment* of A and viceversa.

System separable and uncorrelated from its environment. If, at a given instant of time, two systems A and B are such that the force field produced by B is vanishing in the region of space occupied by A and viceversa, then we say that A and B are *separable* at that instant. The energy of a system A is defined (see Section 3) only for the states of A such that A is separable from its environment. Consider, for instance, the following simple example from mechanics. Let A and B be rigid bodies in deep space, far away from any other object and subjected to a mutual gravitational force. Then, the potential energy of the composite system AB is defined, but that of A and of B is not. For a system A which is separable from its environment, any change in either gravitational, or electric, or magnetic field in the region of space occupied by the system is due to a change of this region, i.e., to a displacement of the system.

If, at a given instant of time, two systems A and B are such that the outcomes of the measurements performed on B are statistically independent of those of the measurements performed on A , and viceversa, we say that A and B are *uncorrelated from each other* at that instant. The entropy of a system A is defined in this paper only for the states of A such that A is separable and uncorrelated from its environment.

Process. We call *process* of a system A from state A_1 to state A_2 the time evolution of the isolated system AB from $(AB)_1$ (with A in state A_1) to $(AB)_2$ (with A in state A_2), where B is the environment of A .

Reversible process. A process of A is *reversible* if the isolated system AB can undergo a time evolution which restores it in its initial state $(AB)_1$. A process of a system A is called a *cycle* for A if the final state A_2 coincides with the initial state A_1 . A cycle for A is not necessarily a cycle for AB .

Weight process. An *elementary mechanical system* is a system such that the only admissible change of state for it is a space translation in a uniform external force field; an example is a particle which can only change its height in a uniform external gravitational field. A process of a system A from state A_1 to A_2 , such that both in A_1 and in A_2 system A is separable

from its environment, is a *weight process* for A if the only net effect of the process in the environment of A is the change of state of an elementary mechanical system.

Equilibrium states. An *equilibrium* state of a system is a state such that the system is separable, the state does not vary with time, and it can be reproduced while the system is isolated. An equilibrium state of a closed system A in which A is uncorrelated from its environment B , is called a *stable equilibrium state* if it cannot be modified by any process between states in which A is separable and uncorrelated from its environment such that neither the geometrical configuration of the walls which bind the regions of space \mathcal{R}^A where the constituents of A are contained, nor the state of the environment B of A have net changes. Two systems, A and B , are in *mutual stable equilibrium* if the composite system AB (*i.e.*, the union of both systems) is in a stable equilibrium state.

Weight polygonal and work in a weight polygonal. Consider an ordered set of n states of a closed system A , (A_1, A_2, \dots, A_n) , such that in each of these states A is separable from its environment. If $n - 1$ weight processes exist, which interconnect A_1 and A_2, \dots, A_{n-1} and A_n , regardless of the direction of each process, we say that A_1 and A_n can be interconnected by a *weight polygonal*. For instance, if weight processes $A_1 \xrightarrow{w} A_2$ and $A_3 \xrightarrow{w} A_2$ exist for A , we say that $A_1 \xrightarrow{w} A_2 \xleftarrow{w} A_3$ is a weight polygonal for A from A_1 to A_3 . We call work done by A in a weight polygonal from A_1 to A_n the sum of the works done by A in the weight processes with direction from A_1 to A_n and the opposites of the works done by A in the weight processes with direction from A_n to A_1 (Zanchini 1986, 1988). The work done by A in a weight polygonal from A_1 to A_n will be denoted by $W_{1n}^{A \xrightarrow{wp}}$; its opposite will be called work received by A in a weight polygonal from A_1 to A_n and will be denoted by $W_{1n}^{A \xleftarrow{wp}}$. Clearly, for a given weight polygonal, $W_{1n}^{A \xleftarrow{wp}} = -W_{1n}^{A \xrightarrow{wp}} = W_{n1}^{A \xrightarrow{wp}}$. For the example of weight polygonal $A_1 \xrightarrow{w} A_2 \xleftarrow{w} A_3$ considered above, we have

$$W_{13}^{A \xrightarrow{wp}} = W_{12}^{A \rightarrow} - W_{32}^{A \rightarrow}. \quad (1)$$

3. Postulates and Assumptions

In this paper, we call *Postulates* the axioms which have a completely general validity and *Assumptions* the additional axioms whose domain of validity could be completely general or not, and identifies the domain of validity of our treatment. In this section, we list at once all the Postulates and, for ease of reference, also a preview of the Assumptions. However, the assumptions require concepts and notation that we introduce later. Therefore, they will acquire meaning and will be repeated along our deductive development by introducing them immediately before they become necessary for the subsequent logical development. This approach allows us to emphasize which results require which assumptions.

Postulate 1. Every pair of states (A_1, A_2) of a closed system A , such that A is separable from its environment in both states, can be interconnected by means of a weight polygonal for A . The works done by a system in any two weight polygonals between the same initial and final states are identical.

Remark. Zanchini (1986) has proved that, in sets of states where sufficient conditions of interconnectability by weight processes hold, Postulate 1 can be proved as a consequence

of the traditional form of the First Law, which concerns weight processes (or adiabatic processes).

Postulate 2. Among all the states of a system A such that the constituents of A are contained in a given set of regions of space \mathbf{R}^A , there is a stable equilibrium state for every value E^A of the energy of A .

Postulate 3. Starting from any state in which the system is separable from its environment, a closed system A can be changed to a stable equilibrium state with the same energy by means of a zero work weight process for A in which the regions of space occupied by the constituents of A have no net changes.

Postulate 4. There exist systems, called normal systems, whose energy has no upper bound. Starting from any state in which the system is separable from its environment, a normal system A can be changed to a non-equilibrium state with arbitrarily higher energy (in which A is separable from its environment) by means of a weight process for A in which the regions of space occupied by the constituents of A have no net changes.

Remark. The restriction to normal closed systems is adopted here in the interest of simplicity, in order to focus the attention of the reader on the main result of the paper, namely that of avoiding the use of the concept of thermal reservoir in the foundations of thermodynamics. The extension of the treatment to *special systems* and *open systems* will be presented elsewhere.

Assumption 1. For any given pair of states (A_1, A_2) of any closed system A such that A is separable and uncorrelated from its environment, it is always possible to find or to include in the environment of A a system B which has a stable equilibrium state B_{se1} such that the states A_1 and A_2 can be interconnected by means of a reversible weight process for AB , standard with respect to B , in which system B starts from state B_{se1} .

Assumption 2. The function $f_{11}^{B \rightarrow C}(E^B)$ defined (see Lemma 2, below) through the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}, \Pi_{XCrev}^{C_{se1}})\}$ (also defined in Lemma 2, below) is differentiable in E_{se1}^B ; in symbols

$$\lim_{E^B \rightarrow E_{se1}^B} \frac{f_{11}^{B \rightarrow C}(E^B) - f_{11}^{B \rightarrow C}(E_{se1}^B)}{E^B - E_{se1}^B} = \left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B}.$$

Assumption 3. For every system B and every choice of the regions of space \mathbf{R}^B occupied by the constituents of B , the temperature of the stable equilibrium states of B (as defined in Section 5, below) is a continuous function of the energy of B and is vanishing only in the stable equilibrium state with the lowest energy for the given regions of space \mathbf{R}^B .

In the last section of the paper we extend our operational definition of entropy to a broader class of system models by relaxing Assumption 1 as follows.

Relaxed Assumption 1. Any given state A_1 of any closed system A such that A is separable and uncorrelated from its environment, either belongs to a single set Σ_A where every pair of states fulfills Assumption 1 or it can be an intermediate state of at least a composite weight process for A that connects two states of the set Σ_A .

4. Definition of energy for a closed system.

Let (A_1, A_2) be any pair of states of a system A , such that A is separable from its environment in both states. We call *energy difference* between states A_2 and A_1 the work received by A in any weight polygonal from A_1 to A_2 , expressed as

$$E_2^A - E_1^A = -W_{12}^{A \xrightarrow{\text{wp}}} = W_{12}^{A \xleftarrow{\text{wp}}}. \quad (2)$$

Postulate 1 implies the following consequences:

- (a) the energy difference between two states A_2 and A_1 depends only on the states A_1 and A_2 ;
 (b) (*additivity of energy differences*) consider a pair of states $(AB)_1$ and $(AB)_2$ of a composite system AB , and denote by A_1, B_1 and A_2, B_2 the corresponding states of A and B ; then, if A , B and AB are separable from their environment in the states considered,

$$E_2^{AB} - E_1^{AB} = E_2^A - E_1^A + E_2^B - E_1^B ; \quad (3)$$

- (c) (*energy is a property*) let A_0 be a reference state of a system A , in which A is separable from its environment, to which we assign an arbitrarily chosen value of energy E_0^A ; the value of the energy of A in any other state A_1 in which A is separable from its environment is determined uniquely by

$$E_1^A = E_0^A + W_{01}^{A \xleftarrow{\text{wp}}}, \quad (4)$$

where $W_{01}^{A \xleftarrow{\text{wp}}}$ is the work received by A in any weight polygonal for A from A_0 to A_1 . Simple proofs of these consequences are available in Zanchini (1986), and will not be repeated here.

Remark. The additivity of energy implies that the union of two or more normal systems, each separable from its environment, is a normal system to which Postulate 4 applies. In traditional treatments of thermodynamics only normal systems are considered, without an explicit mention of this restriction. Moreover, Postulate 4 is *not stated, but it is used*, for example in theorems where one says that any amount of work can be transferred to a thermal reservoir by a stirrer. Any system whose constituents have translational, rotational or vibrational degrees of freedom is a normal system. On the other hand, quantum theoretical model systems, such as spins, qubits, qudits, etc., whose energy is bounded also from above, are special systems.

5. Definition of temperature of a stable equilibrium state

Lemma 1. Uniqueness of the stable equilibrium state for a given value of the energy.

There can be no pair of different stable equilibrium states of a closed system A with identical regions of space \mathbf{R}^A and the same value of the energy E^A . The proof is in Footnote 2.

Theorem 1. Impossibility of a Perpetual Motion Machine of the Second Kind (PMM2).

If a normal system A is in a stable equilibrium state, it is impossible to lower its energy by means of a weight process for A in which the regions of space occupied by the constituents of A have no net change. The proof is in Footnote 3.

Remark. Kelvin-Planck statement of the Second Law. As noted by Hatsopoulos and Keenan (1965) and Gyftopoulos and Beretta (2005, p.64), the impossibility of a PMM2, which is also known as the *Kelvin-Planck statement of the Second Law*, is a corollary of the definition of stable equilibrium state, provided that we adopt the (usually implicit) restriction to normal systems.

Definition. Weight process for AB , standard with respect to B .

Given a pair of states (A_1, A_2) of a system A , such that A is separable from its environment, and a system B in the environment of A , we call *weight process for AB , standard with respect to B* a weight process $A_1 B_{se1} \xrightarrow{W} A_2 B_{se2}$ for the composite system AB in which the end states of A are the given states A_1 and A_2 , and the end states of B are stable equilibrium states with identical regions of space \mathbf{R}^B . For a weight process for AB , standard with respect to B , we denote the final energy of system B by the symbol $E_{se2}^B |_{A_1 A_2}^{sw, B_{se1}}$ or, if the process is reversible, $E_{se2rev}^B |_{A_1 A_2}^{sw, B_{se1}}$ (when the context allows it, we simply denote them by E_{se2}^B and E_{se2rev}^B , respectively).

Remark. The term “standard with respect to B ” is a shorthand to express the conditions that: 1) the end states of B are stable equilibrium, and 2) the regions of space \mathbf{R}_{se1}^B and \mathbf{R}_{se2}^B are identical. The regions of space \mathbf{R}_1^A and \mathbf{R}_2^A , instead, need not be identical.

Assumption 1. For any given pair of states (A_1, A_2) of any closed system A such that A is separable and uncorrelated from its environment, it is always possible to find or to include in the environment of A a system B which has a stable equilibrium state B_{se1} such that the

²**Proof of Lemma 1.** Since A is closed and in any stable equilibrium state it is separable and uncorrelated from its environment, if two such states existed, by Postulate 3 the system could be changed from one to the other by means of a zero-work weight process, with no change of the regions of space occupied by the constituents of A and no change of the state of the environment of A . Therefore, neither would satisfy the definition of stable equilibrium state. \square

³**Proof of Theorem 1.** Suppose that, starting from a stable equilibrium state A_{se} of A , by means of a weight process Π_1 with positive work $W^{A \rightarrow} = W > 0$, the energy of A is lowered and the regions of space \mathbf{R}^A occupied by the constituents of A have no net change. On account of Postulate 4, it would be possible to perform a weight process Π_2 for A in which its regions of space \mathbf{R}^A have no net change, the weight M is restored to its initial state so that the positive amount of energy $W^{A \leftarrow} = W > 0$ is supplied back to A , and the final state of A is a non-equilibrium state, namely, a state clearly different from A_{se} . Thus, the composite zero-work weight process (Π_1, Π_2) would violate the definition of stable equilibrium state. \square

states A_1 and A_2 can be interconnected by means of a reversible weight process for AB , standard with respect to B , in which system B starts from state $B_{\text{se}1}$.

Remark. If, for a given pair of states (A_1, A_2) , a stable equilibrium state $B_{\text{se}1}$ of B fulfills Assumption 1, then any other stable equilibrium state of B with the same regions of space and with an energy value higher than that of $B_{\text{se}1}$ fulfills Assumption 1, as well. Therefore, for a given pair of states (A_1, A_2) of a system A and a selected system B , there exist infinite different choices for $B_{\text{se}1}$.

Remark. Since Postulates 1 to 3 can be considered as having a completely general validity, our new operational definition of entropy for a normal and closed system A applies to any set of states such that A is separable and uncorrelated from its environment, and for which the crucial Assumption 1 holds for every pair of states in the set. In the next remark, we show that in quantum statistical mechanics (QSM) Assumption 1 holds for all the stable equilibrium states and for a large class of nonequilibrium states, for both large and few-particle systems. Moreover, in subsequent remarks we also demonstrate the full compatibility of our construction with the general framework of QSM.

Remark. Plausibility of Assumption 1 in the framework of quantum statistical mechanics. Let us illustrate the range of validity of Assumption 1 within the framework of quantum statistical mechanics by showing that a broad (albeit not all-inclusive) class of pairs (A_1, A_2) of nonequilibrium states of any system A can be interconnected by a quantum mechanical unitary process (i.e., a reversible weight process) of a composite system AB such that the initial and final states of a system B are stable equilibrium states.

To this end, given the system A , consider a system B with Hilbert space of equal dimensionality ($\dim \mathcal{H}_B = \dim \mathcal{H}_A$) but different Hamiltonian operator ($H^B \neq H^A$), and consider the states $B_{\text{se}1} = \rho_1^B = \exp(-\ln Z_1^B - \beta_1 H^B)$ and $B_{\text{se}2} = \rho_2^B = \exp(-\ln Z_2^B - \beta_2 H^B)$ where ρ denotes the density operator (i.e., the state representative in QSM) and Z the partition function defined by the condition $\text{Tr}\rho = 1$.

Next, consider the eigenvalue problems $H^A|\psi_j^A\rangle = \varepsilon_j^A|\psi_j^A\rangle$ and $H^B|\psi_j^B\rangle = \varepsilon_j^B|\psi_j^B\rangle$ and assume that the index j ranks energy eigenvalues in increasing order for both A and B . Finally, consider the states of A constructed as follows $A_1 = \rho_1^A = \sum_j \exp(-\ln Z_2^A - \beta_2 \varepsilon_j^A)|\psi_j^A\rangle\langle\psi_j^A|$ and $A_2 = \rho_2^A = \sum_j \exp(-\ln Z_1^A - \beta_1 \varepsilon_j^A)|\psi_j^A\rangle\langle\psi_j^A|$. These states are nonequilibrium states for A because the ε_j^B 's are not the eigenvalues of H^A but those of $H^B \neq H^A$. Notice, however, that they commute with H^A and have decreasing diagonal elements (probabilities), so that $E_1^A = \text{Tr}\rho_1^A H^A$ is minimal among the states with $-k\text{Tr}\rho \ln \rho = -k\text{Tr}\rho_1^A \ln \rho_1^A = S_1^A$ and $E_2^A = \text{Tr}\rho_2^A H^A$ is minimal among the states with $-k\text{Tr}\rho \ln \rho = -k\text{Tr}\rho_2^A \ln \rho_2^A = S_2^A$. From these nonequilibrium states we can access, via unitary evolutions of A (i.e., by means of reversible weight processes for A), a large number of nonequilibrium states corresponding to all possible rearrangement of the order of the diagonal elements in the H^A representation. Now, we need only show that the process $\rho_1^A \otimes \rho_1^B \rightarrow \rho_2^A \otimes \rho_2^B$ can be done by means of a unitary evolution for the composite system AB . This is a straightforward consequence of the well-known fact (see, e.g., von Neumann 1955, p.351 and Hatsopoulos

and Gyftopoulos 1976, p.136) that by designing a suitable time dependent Hamiltonian that starts and ends with the initial, separable one ($H^{AB} = H^A \otimes I^A + I^B \otimes H^B$) it is possible to change any density operator unitarily into any other one with the same set of eigenvalues. Indeed, the eigenvalues of ρ_1^A , ρ_2^B , ρ_2^A , and ρ_1^B are, respectively, $(p_j)_1^A = (p_j)_2^B = \exp(-\ln Z_2^B - \beta_2 \epsilon_j^B)$ and $(p_j)_2^A = (p_j)_1^B = \exp(-\ln Z_1^B - \beta_1 \epsilon_j^B)$. Therefore, by our particular construction, operators $\rho_1^A \otimes \rho_1^B$ and $\rho_2^A \otimes \rho_2^B$ have the same eigenvalues $(p_{ij})_1^{AB} = (p_i)_1^A (p_j)_1^B = (p_{ij})_2^{AB} = (p_i)_2^A (p_j)_2^B$.

It is noteworthy that if we repeat the above considerations by using a system B identical to A , i.e., for identical Hamiltonian operators ($H^B = H^A$), then states A_1 and A_2 are stable equilibrium and we confirm that, in the QSM context, Assumption 1 is always fulfilled for all pairs of stable equilibrium states.

In summary, in a QSM context in which only unitary protocols are conceivable, the domain of validity of Assumption 1 includes all but only: (1) the (stable equilibrium) canonical density operators of A ; and (2) the pairs of nonequilibrium density operators of A each of which can be unitarily reduced to a form with eigenvalues that are canonically distributed with respect to the same but otherwise arbitrary set of energy levels ϵ_j^B (not necessarily the eigenvalues of H^A).

However, if one accepts that, at least in some limiting sense, non-unitary protocols may be within feasible reach or are at least conceivable, then the domain of validity can be broadened to include all nonequilibrium density operators. This would be the case if we could smoothly control each eigenvalue of the given ρ_1^A and ρ_2^A so that each of them follows the path of steepest energy descent (Beretta 2008, Eq.75) to the corresponding canonical density operator with entropy $-k\text{Tr}\rho_1^A \ln \rho_1^A$ and $-k\text{Tr}\rho_2^A \ln \rho_2^A$, respectively.

Theorem 2. Given a pair of states (A_1, A_2) of a system A such that A is separable and uncorrelated from its environment, a system B in the environment of A , and an initial stable equilibrium state $B_{\text{se}1}$, among all the weight processes for AB , standard with respect to B , in which A goes from A_1 to A_2 and B begins in state $B_{\text{se}1}$, the energy $E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$ of system B in its final state has a lower bound, $E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$, which is reached if and only if the process is reversible. Moreover, for all such reversible processes, system B ends in the same stable equilibrium state $B_{\text{se}2\text{rev}}$. The proof is in Footnote 4.

⁴**Proof of Theorem 2.** Consider a weight process for AB , standard with respect to B , $\Pi_{AB} = A_1 B_{\text{se}1} \xrightarrow{w} A_2 B_{\text{se}2}$, a reversible weight processes for AB , standard with respect to B , $\Pi_{AB\text{rev}} = A_1 B_{\text{se}1} \xrightarrow{\text{wrev}} A_2 B_{\text{se}2\text{rev}}$, and the corresponding final energies of B , respectively, $E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$ and $E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$. We will prove that:

- (a) $E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}} \leq E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$;
- (b) if also Π_{AB} is reversible, then $E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}} = E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$, and the end stable equilibrium state of B is the same, i.e., $B_{\text{se}2} = B_{\text{se}2\text{rev}}$;
- (c) if $E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}} = E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$, then also Π_{AB} is reversible.

Proof of (a). Let us suppose, *ab absurdo*, that the energy of B in state $B_{\text{se}2}$ is lower than that in state $B_{\text{se}2\text{rev}}$. Then, the composite process $(-\Pi_{AB\text{rev}}, \Pi_{AB})$ would be a weight process for B in which, starting from the stable equilibrium state $B_{\text{se}2\text{rev}}$, the energy of B is lowered and its regions of space have no net changes, in contrast with Theorem 1. Therefore, $E_{\text{se}2\text{rev}}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}} \leq E_{\text{se}2}^B |_{A_1 A_2}^{\text{sw}, B_{\text{se}1}}$.

Theorem 3. Consider a pair of states (A_1, A_2) of a system A such that A is separable and uncorrelated from its environment, and two systems in the environment of A , B and C , in given initial stable equilibrium states B_{se1} and C_{se1} . Let Π_{ABrev} and Π_{ACrev} be reversible weight processes for AB and for AC , both from A_1 to A_2 and standard with respect to B and C respectively, with the given initial states B_{se1} and C_{se1} of B and C ; let E^B denote, for shorthand, the final energy $E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}}$ of B in process Π_{ABrev} and let E^C denote the final energy $E_{se2rev}^C |_{A_1A_2}^{sw, C_{se1}}$ of C in process Π_{ACrev} . Then, if $E^B - E_{se1}^B$ is vanishing, $E^C - E_{se1}^C$ is vanishing as well; if $E^B - E_{se1}^B$ is non vanishing, $E^C - E_{se1}^C$ is non vanishing and the ratio $(E^B - E_{se1}^B)/(E^C - E_{se1}^C)$ is positive. The proof is in Footnote 5.

Lemma 2. Consider a pair of systems, B and C , a pair of stable equilibrium states of these systems, B_{se1} and C_{se1} , and a system X in the environment of BC with an initial state X_1 such that: every stable equilibrium state of B with the same regions of space as B_{se1} can be interconnected with B_{se1} by a reversible weight process for XB starting from (X_1, B_{se1}) ; every stable equilibrium state of C with the same regions of space as C_{se1} can be interconnected with C_{se1} by a reversible weight process for XC starting from (X_1, C_{se1}) .

Proof of (b). If also process Π_{AB} is reversible, then, in addition to $E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}} \leq E_{se2}^B |_{A_1A_2}^{sw, B_{se1}}$, also the relation $E_{se2}^B |_{A_1A_2}^{sw, B_{se1}} \leq E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}}$ must hold by virtue of the proof of a) just given and, therefore, $E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}} = E_{se2}^B |_{A_1A_2}^{sw, B_{se1}}$. On account of Postulate 2 and Lemma 1, the final value of the energy of B determines a unique final stable equilibrium state of B ; therefore $B_{se2} = B_{se2rev}$.

Proof of (c). Let Π_{AB} be such that $E_{se2}^B |_{A_1A_2}^{sw, B_{se1}} = E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}}$. Then, the final states B_{se2} and B_{se2rev} have the same energy and, being stable equilibrium states, by Lemma 1 they must coincide. Thus, the composite process $(\Pi_{AB}, -\Pi_{ABrev})$ is a cycle for the isolated system ABC , where C is the environment of AB , where the only effect is the return of the weight to its initial position. As a consequence, being a part of a cycle of the isolated system ABC , process Π_{AB} is reversible. \square

⁵**Proof of Theorem 3.** Assume that $E^B - E_{se1}^B$ is vanishing and that $E^C - E_{se1}^C$ is positive, and consider the composite process $(\Pi_{ABrev}, -\Pi_{ACrev})$; this would be a reversible weight process for C in which the energy change of C is negative, the regions of space occupied by C do not change and the initial state of C is a stable equilibrium state, in contrast with Theorem 1. Assume now that $E^B - E_{se1}^B$ is vanishing and that $E^C - E_{se1}^C$ is negative, and consider the composite process $(\Pi_{ACrev}, -\Pi_{ABrev})$; this would be a reversible weight process for C in which the energy change of C is negative, the regions of space occupied by C do not change and the initial state of C is a stable equilibrium state, in contrast with Theorem 1. Then, if $E^B - E_{se1}^B$ is vanishing, $E^C - E_{se1}^C$ is vanishing as well.

Assume now that the energy change of B is negative, i.e., $E^B - E_{se1}^B < 0$. Clearly, the energy change of C cannot be zero, because this would imply $E^B - E_{se1}^B = 0$. Suppose that the energy change of C is positive, $E^C - E_{se1}^C > 0$, and consider the composite process $(\Pi_{ABrev}, -\Pi_{ACrev})$. In this process, which is a cycle for A , system BC would have performed a positive work, given (energy balance for BC) by the sum of two positive addenda, namely $W = -(E^B - E_{se1}^B) + (E^C - E_{se1}^C)$. On account of Postulates 4 and 3, one could supply back to system C a positive work amount equal to $(E^C - E_{se1}^C)$ and restore C to its initial state C_{se1} by means of a composite weight process $\Pi_C = C_{se2} \xrightarrow{w} C_3 \xrightarrow{w} C_{se1}$ where C_3 has energy $E_{C_3}^C = E_{se1}^C$. Thus, the composite process $(\Pi_{ABrev}, -\Pi_{ACrev}, \Pi_C)$ would be a again a weight process for B which violates Theorem 1. Therefore, if $E^B - E_{se1}^B$ is negative, $E^C - E_{se1}^C$ is negative as well.

Let us assume now that, in process Π_{ABrev} , the energy change of B is positive. Then, in the reverse process $-\Pi_{ABrev}$, the energy change of B is negative and, as we have just proved, the energy change of C in the reverse process $-\Pi_{ACrev}$ must be negative as well. Therefore, in process Π_{ACrev} , the energy change of C is positive. \square

Denote by $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$ the set of all the pairs of reversible weight processes for XB and for XC , standard with respect to B and C and with initial states (X_1, B_{se1}) and (X_1, C_{se1}) respectively, and such that for each pair of processes, the final state X_2 of X is the same. Let $\{(B_{se2}; C_{se2})\}$ the set of pairs of final states of B and C which one obtains by the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$, and let $\{(E_{se2}^B; E_{se2}^C)\}$ be the corresponding values of the energy of B and C . Then, the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$ determines a single valued and invertible function from the set $\{E_{se2}^B\}$ to the set $\{E_{se2}^C\}$,

$$E^C = f_{11}^{B \rightarrow C}(E^B) , \tag{5}$$

which is independent on the choice of system X and on the initial state X_1 used to construct the set of processes $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$. The proof is in Footnote 6.

Remark. Lemma 2 plays a key role in the new definition of temperature that we propose below. On the other hand, the statement and the proof of Lemma 2 require a considerable effort to be fully understood. Therefore, to help the reader, we show here that the existence of the function $f_{11}^{B \rightarrow C}(E^B)$, as well as its differentiability in E_{se1}^B , that we state later in Assumption 2, can be easily shown in the usual framework of thermodynamics *a posteriori*, i.e., once temperature and entropy are defined. Consider systems B and C in their initial stable equilibrium states B_{se1} and C_{se1} , with energy values E_{se1}^B and E_{se1}^C (and corresponding temperatures T_{se1}^B and T_{se1}^C) and pairs of reversible weight processes for XB and for XC , standard with respect to B and C , with initial state X_1 of the auxiliary system X and such that for each pair of processes, the final state X_2 of X is the same, so that the entropy change of X is the same. In each pair of such processes, the entropy change ΔS of C is equal to that of B , because both are equal to the opposite of the entropy change of X . Moreover, the end states of B and C are stable equilibrium states and the regions of space occupied by the systems do not change. For a closed system that occupies a fixed region of space, each stable equilibrium state is determined uniquely either by the value of the energy, or by that of the entropy, since entropy is a strictly increasing function of the energy. Therefore, the

⁶**Proof of Lemma 2.** Choose a system X and an initial state X_1 of X , and consider a pair of reversible weight processes $(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})$, which belongs to the set $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$. Let X_2, B_{se2} and C_{se2} be the final states of X, B and C for this pair of processes. Choose now a system X' and an initial state X'_1 of X' , and consider a pair of reversible weight processes $(\Pi_{X'Brev}^{B_{se1}}; \Pi_{X'Crev}^{C_{se1}})$, which belongs to the set $\{(\Pi_{X'Brev}^{B_{se1}}; \Pi_{X'Crev}^{C_{se1}})\}$. Let X'_2, B_{se3} and C_{se3} be the final states of X, B and C for this pair of processes. We will prove that, if B_{se3} coincides with B_{se2} , then also C_{se3} coincides with C_{se2} , so that the correspondence between the final stable equilibrium states of B and C is not affected by either the choice of the auxiliary system, X or X' , or the choice of the initial state of the auxiliary system.

Consider the composite system $XX'BC$, in the initial state $X_1X'_2B_{se1}C_{se2}$, and consider the composite process $\Pi = (\Pi_{XBrev}^{B_{se1}}; -\Pi_{XCrev}^{C_{se1}}, -\Pi_{X'Brev}^{B_{se1}}; \Pi_{X'Crev}^{C_{se1}})$, where $-\Pi_{XCrev}^{C_{se1}}$ is the reverse of $\Pi_{XCrev}^{C_{se1}}$ and $-\Pi_{X'Brev}^{B_{se1}}$ is the reverse of $\Pi_{X'Brev}^{B_{se1}}$. As easily verified, $\Pi = X_1X'_2B_{se1}C_{se2} \xrightarrow{wrev} X_2X'_2B_{se2}C_{se2} \xrightarrow{wrev} X_1X'_2B_{se2}C_{se1} \xrightarrow{wrev} X_1X'_1B_{se1}C_{se1} \xrightarrow{wrev} X_1X'_2B_{se1}C_{se3}$, therefore, the final state of the composite system $XX'BC$, after process Π , is $X_1X'_2B_{se1}C_{se3}$. Therefore, Π is a reversible weight process for C in which the regions of space occupied by the constituents of C have no net change. If the energy of C in state C_{se3} were lower than that in the initial state C_{se2} , then Π would violate Theorem 1. If the energy of C in state C_{se3} were higher than that in the initial state C_{se2} , then the reverse of Π would violate Theorem 1. Therefore, the energy of C in state C_{se3} must coincide with the energy of C in state C_{se2} , i.e., on account of Postulate 2 and Lemma 1, the state C_{se3} must coincide with C_{se2} . \square

final energy values E^B and E^C are determined uniquely by ΔS , so that the latter determines a one-to-one correspondence between the final energy values E^B and E^C , that we denote by $E^C = f_{11}^{B \rightarrow C}(E^B)$. In addition, when ΔS is very small, also the energy changes ΔE^B and ΔE^C are very small, and one has $\Delta E^B \approx T_{se1}^B \Delta S$, $\Delta E^C \approx T_{se1}^C \Delta S$, so that $\Delta E^C \approx T_{se1}^C \Delta E^B / T_{se1}^B$, and by considering the limit for $\Delta S \rightarrow 0$ one obtains

$$\lim_{\Delta S \rightarrow 0} \frac{\Delta E^C(\Delta S)}{\Delta E^B(\Delta S)} = \lim_{\Delta E^B \rightarrow 0} \frac{\Delta E^C(\Delta E^B)}{\Delta E^B} = \frac{T_{se1}^C}{T_{se1}^B}. \tag{6}$$

In another remark, reported after our definition of temperature, we show, as an example, how the function $f_{11}^{B \rightarrow C}(E^B)$ is construed in the framework of quantum statistical mechanics (Eq. 23).

Lemma 3. For a given pair of systems, B and C , consider an arbitrary pair of stable equilibrium states (B_{se1}, C_{se1}) and the set of processes which defines the function $E^C = f_{11}^{B \rightarrow C}(E^B)$ according to Lemma 2. Select another arbitrary stable equilibrium state B_{se2} of system B and let C_{se2} be the stable equilibrium state of system C such that $E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B)$. Denote by $E^C = f_{22}^{B \rightarrow C}(E^B)$ the function defined by the set of reversible processes $\{(\Pi_{XB_{se2}}^{B_{se2}} \cdot \Pi_{XC_{se2}}^{C_{se2}})\}$ according to Lemma 2. Then we have the identity

$$f_{11}^{B \rightarrow C}(E^B) = f_{22}^{B \rightarrow C}(E^B) \text{ for every } E^B. \tag{7}$$

The proof is in Footnote 7.

Corollary 1. The function $f_{11}^{B \rightarrow C}(E^B)$ defined through the set of pairs of processes

$$\{(\Pi_{XB_{se1}}^{B_{se1}} \cdot \Pi_{XC_{se1}}^{C_{se1}})\}$$

is strictly increasing. The proof is in Footnote 8.

Remark. Since the function $f_{11}^{B \rightarrow C}(E^B)$ is strictly increasing, it is invertible. The inverse of the function

$$E^C = f_{11}^{B \rightarrow C}(E^B), \tag{8}$$

will be denoted by

$$E^B = f_{11}^{C \rightarrow B}(E^C). \tag{9}$$

⁷**Proof of Lemma 3.** Consider an arbitrary stable equilibrium state of system B with energy E^B and denote it by B_{se3} , i.e. $E_{se3}^B = E^B$, and let C_{se3} be the stable equilibrium state of system C such that $E_{se3}^C = f_{22}^{B \rightarrow C}(E^B)$. Then, the pair of composite processes $(X_1 B_{se1} \xrightarrow{\text{wrev}} X_2 B_{se2} \xrightarrow{\text{wrev}} X_3 B_{se3}, X_1 C_{se1} \xrightarrow{\text{wrev}} X_2 C_{se2} \xrightarrow{\text{wrev}} X_3 C_{se3})$ exists because $E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B)$ and $E_{se3}^C = f_{22}^{B \rightarrow C}(E_{se3}^B)$, and it clearly belongs to the set of pairs of processes which defines the function $E^C = f_{11}^{B \rightarrow C}(E^B)$, therefore, $E_{se3}^C = f_{11}^{B \rightarrow C}(E_{se3}^B)$. \square

⁸**Proof of Corollary 1.** Consider the pairs of stable equilibrium states (B_{se2}, C_{se2}) and (B_{se3}, C_{se3}) , such that $E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B)$, $E_{se3}^C = f_{11}^{B \rightarrow C}(E_{se3}^B)$, and $E_{se3}^B > E_{se2}^B$. We will prove that $E_{se3}^C > E_{se2}^C$, i.e., $f_{11}^{B \rightarrow C}(E_{se3}^B) > f_{11}^{B \rightarrow C}(E_{se2}^B)$.

Consider the pair of composite processes $(X_2 B_{se2} \xrightarrow{\text{wrev}} X_1 B_{se1} \xrightarrow{\text{wrev}} X_3 B_{se3}, X_2 C_{se2} \xrightarrow{\text{wrev}} X_1 C_{se1} \xrightarrow{\text{wrev}} X_3 C_{se3})$, which exists because $E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B)$ and $E_{se3}^C = f_{11}^{B \rightarrow C}(E_{se3}^B)$. In this pair of processes, the energy change of B , $E_{se3}^B - E_{se2}^B$, is positive. On account of Theorem 3, also the energy change of C must be positive, i.e., $E_{se3}^C > E_{se2}^C$. \square

The domain of function $f_{11}^{B \rightarrow C}$ is the set of all the energy values of system B compatible with the regions of space occupied by the constituents of B in state B_{se1} . The domain of function $f_{11}^{C \rightarrow B}$ is the set of all the energy values of system C compatible with the regions of space occupied by the constituents of C in state C_{se1} .

Lemma 4. Consider three systems $B, C,$ and $R,$ three stable equilibrium states $B_{se1}, C_{se1},$ and $R_{se1},$ and the functions $E^R = f_{11}^{B \rightarrow R}(E^B), E^C = f_{11}^{R \rightarrow C}(E^R),$ and $E^C = f_{11}^{B \rightarrow C}(E^B)$ defined as in Lemma 2. Then,

$$f_{11}^{B \rightarrow C}(E^B) = f_{11}^{R \rightarrow C}(f_{11}^{B \rightarrow R}(E^B)) \quad (10)$$

The proof is in Footnote 9.

Assumption 2. The function $f_{11}^{B \rightarrow C}(E^B)$ defined through the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}, \Pi_{XCrev}^{C_{se1}})\}$ is differentiable in E_{se1}^B ; in symbols

$$\lim_{E^B \rightarrow E_{se1}^B} \frac{f_{11}^{B \rightarrow C}(E^B) - f_{11}^{B \rightarrow C}(E_{se1}^B)}{E^B - E_{se1}^B} = \left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B} \quad (16)$$

Below, in the Remark that follows the definition of temperature, we show that Assumption 2 is fulfilled within the quantum statistical mechanics framework, at least within the range of validity of Assumption 1.

Corollary 2. The inverse function $E^B = f_{11}^{C \rightarrow B}(E^C)$ is differentiable in $E_{se1}^C,$ moreover if

$$\left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B} \neq 0$$

⁹**Proof of Lemma 4.** Consider an auxiliary system $X,$ the pair of states $(X_1, X_2),$ and the three processes $\Pi_{XBrev}^{B_{se1}}, \Pi_{XCrev}^{C_{se1}}, \Pi_{XRrev}^{R_{se1}},$ respectively defined as follows: $\Pi_{XBrev}^{B_{se1}}$ is a reversible weight process for XB with initial and final states X_1 and X_2 for $X,$ and initial state B_{se1} for $B;$ $\Pi_{XCrev}^{C_{se1}}$ is a reversible weight process for XC with initial and final states X_1 and X_2 for $X,$ and initial state C_{se1} for $C;$ $\Pi_{XRrev}^{R_{se1}}$ is a reversible weight process for XR with initial and final states X_1 and X_2 for $X,$ and initial state R_{se1} for $R.$ Let us denote by $E_{se2}^B, E_{se2}^C, E_{se2}^R$ the energy of the final states of B, C and $R,$ respectively. The pair of processes $(\Pi_{XBrev}^{B_{se1}}, \Pi_{XRrev}^{R_{se1}})$ belongs to the set of processes $\{(\Pi_{XBrev}^{B_{se1}}, \Pi_{XRrev}^{R_{se1}})\}$ that defines according to Lemma 2 the function $E^R = f_{11}^{B \rightarrow R}(E^B),$ therefore,

$$E_{se2}^R = f_{11}^{B \rightarrow R}(E_{se2}^B) \quad (11)$$

The pair of processes $(\Pi_{XRrev}^{R_{se1}}, \Pi_{XCrev}^{C_{se1}})$ belongs to the set of processes $\{(\Pi_{XRrev}^{R_{se1}}, \Pi_{XCrev}^{C_{se1}})\}$ that defines according to Lemma 2 the function $E^C = f_{11}^{R \rightarrow C}(E^R),$ therefore,

$$E_{se2}^C = f_{11}^{R \rightarrow C}(E_{se2}^R) \quad (12)$$

The pair of processes $(\Pi_{XBrev}^{B_{se1}}, \Pi_{XCrev}^{C_{se1}})$ belongs to the set of processes $\{(\Pi_{XBrev}^{B_{se1}}, \Pi_{XCrev}^{C_{se1}})\}$ that defines according to Lemma 2 the function $E^C = f_{11}^{B \rightarrow C}(E^B),$ therefore,

$$E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B) \quad (13)$$

From (11) and (12) it follows that

$$E_{se2}^C = f_{11}^{R \rightarrow C}(f_{11}^{B \rightarrow R}(E_{se2}^B)) \quad (14)$$

Comparing (14) and (13) we find

$$f_{11}^{B \rightarrow C}(E_{se2}^B) = f_{11}^{R \rightarrow C}(f_{11}^{B \rightarrow R}(E_{se2}^B)) \quad (15)$$

Equation (10) follows immediately from (15) by repeating the above for all possible choices of the pair of states $(X_1, X_2).$ □

then

$$\left. \frac{df_{11}^{C \rightarrow B}}{dE^C} \right|_{E_{se1}^C} = \frac{1}{\left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B}} \quad (17)$$

The proof is in Footnote 10.

Definition. Temperature of a stable equilibrium state. Let R be a *reference system*, and let R_{se1} be a *reference stable equilibrium state* of R . Both R and R_{se1} are fixed once and for all, and a positive real number, T_{se1}^R , chosen arbitrarily, is associated with R_{se1} and called *temperature* of R_{se1} . Let B be any system, and B_{se1} any stable equilibrium state of B .

Let us consider the set of pairs of processes $\{(\Pi_{XRrev}^{R_{se1}}; \Pi_{XBrev}^{B_{se1}})\}$, where $\Pi_{XRrev}^{R_{se1}}$ is any reversible weight process for XR standard with respect R and with initial state R_{se1} , $\Pi_{XBrev}^{B_{se1}}$ is any reversible weight process for XB standard with respect B and with initial state B_{se1} , and X is a system which can be chosen and changed arbitrarily, as well as the initial state of X . On account of Lemma 2 and of Assumption 2, the set of pairs of processes $\{(\Pi_{XRrev}^{R_{se1}}; \Pi_{XBrev}^{B_{se1}})\}$ defines a single valued and invertible function $f_{11}^{R \rightarrow B}(E^R)$, from the energy values of the stable equilibrium states of R with the same regions of space as R_{se1} to the energy values of the stable equilibrium states of B with the same regions of space as B_{se1} , which is differentiable in E_{se1}^R . We define as *temperature* of system B in the stable equilibrium state B_{se1} the quantity T_{se1}^B such that

$$\frac{T_{se1}^B}{T_{se1}^R} = \lim_{E^R \rightarrow E_{se1}^R} \frac{f_{11}^{R \rightarrow B}(E^R) - f_{11}^{R \rightarrow B}(E_{se1}^R)}{E^R - E_{se1}^R} = \left. \frac{df_{11}^{R \rightarrow B}}{dE^R} \right|_{E_{se1}^R} \quad (18)$$

On account of Corollary 1, T_{se1}^B is non-negative. Since R and R_{se1} have been fixed once and for all, the temperature is a property of B , defined for all the stable equilibrium states of B . Clearly, the property temperature is defined by Eq. (18) only with respect to the chosen reference state R_{se1} of the reference system R and up to the arbitrary multiplicative constant T_{se1}^R .

Remark. Agreement with quantum statistical mechanics. As an important example, we show that the existence of the single valued function defined in Lemma 2, the differentiability of that function (Assumption 2) and the definition of thermodynamic temperature given by Eq. 18 are in agreement with the standard description of stable equilibrium states in quantum statistical mechanics (QSM).

In QSM, the Hamiltonian operator H of a system defines the canonical density operators that represent the stable equilibrium (maximum von Neumann entropy) states, namely, the one-parameter family $\rho_{se}(\beta) = \exp(-\beta H)/Z(\beta)$, where $Z(\beta) = \text{Tr} \exp(-\beta H)$ is the partition function. As is well known (see, e.g., (von Neumann 1955, p.392) and (Katz 1967, p.45)), $\rho(\beta)$ is the maximizer of the von Neumann entropy functional $S_{vN} = -k \text{Tr} \rho \ln \rho$ subject to the constraints $\text{Tr} \rho = 1$ and $\text{Tr} \rho H = E$, where β is the Lagrange multiplier associated with the latter constraint and is clearly a continuous function of E . The relations

¹⁰**Proof of Corollary 2.** Since Assumption 2 holds for any pair of systems, by exchanging B with C it implies that also the function $f_{11}^{C \rightarrow B}(E^C)$ is differentiable. Equation (17) follows from the theorem on the derivative of the inverse function. \square

$E_{se}(\beta) = -\partial \ln Z(\beta) / \partial \beta$, $S_{vN,se}(\beta) = k\beta E_{se}(\beta) + k \ln Z(\beta)$, $C(\beta) = -k\beta^2 \partial E_{se}(\beta) / \partial \beta = k^2 \beta^2 \partial^2 \ln Z(\beta) / \partial \beta^2 = -\beta \partial S_{vN,se}(\beta) / \partial \beta$ determine the mean energy E , the von Neumann entropy $S_{vN,se}$ and the heat capacity C , respectively, where k is Boltzmann's constant. Since $C(\beta) / k\beta^2$ is positive, relation $E = E_{se}(\beta)$ is monotonic and hence invertible, to yield $\beta = \beta(E)$. Therefore, we may write $S_{vN,se}(E) = kE \beta(E) + k \ln Z(\beta(E))$ and $dS_{vN,se}(E) / dE = k\beta(E)$.

Next, consider the function of E defined by the difference between the von Neumann entropies $S_{vN,se}(E)$ and $S_{vN,se}(E_1)$ of the two stable equilibrium states with energies E and E_1 , respectively. Assuming that E_1 is a fixed value, let us denote this function by

$$h_1(E) = S_{vN,se}(E) - S_{vN,se}(E_1), \tag{19}$$

its derivative by h'_1 , and its inverse by η_1 , so that the inverse function theorem yields the identity

$$\eta'_1(h_1(E)) = \frac{1}{h'_1(\eta_1(h_1(E)))}. \tag{20}$$

Clearly, $h'_1(E) = k\beta(E)$ and indeed $h_1(E)$ is invertible under our Postulate 4 because for normal systems operator H is unbounded from above and, therefore, β is positive and also $S_{vN,se}(E)$ is invertible.

Now, select an initial stable equilibrium state for a system B and one for a system C , and consider the pairs of processes adopted to define the function $f_{11}^{B \rightarrow C}$ in Lemma 2. In each such pair of processes, since the von Neumann entropies of XB and XC do not change and the von Neumann entropy change of X is fixed, it follows that the von Neumann entropy change of C equals that of B , i.e., $S_{vN,se}^C(E^C) - S_{vN,se}^C(E_1^C) = S_{vN,se}^B(E^B) - S_{vN,se}^B(E_1^B)$ and so the relation between the energies of the end (stable equilibrium) states of B and C is such that

$$h_1^C(E^C) = h_1^B(E^B). \tag{21}$$

Using the invertibility of function $h_1(E)$, we may rewrite this relation as

$$E^C = \eta_1^C(h_1^B(E^B)). \tag{22}$$

Equation (22) shows that the single valued function defined by the pairs of processes defined in Lemma 2 exists and is given by

$$E^C = f_{11}^{B \rightarrow C}(E^B) = \eta_1^C(h_1^B(E^B)). \tag{23}$$

It is easily proved that $f_{11}^{B \rightarrow C}(E^B)$ is differentiable. In fact, by applying the chain rule and employing the identity (20) and again Eq. (23), one obtains

$$\frac{d f_{11}^{B \rightarrow C}(E^B)}{dE^B} = \eta_1^C(h_1^B(E^B)) h_1^B(E^B) = \frac{h_1^B(E^B)}{h_1^C(\eta_1^C(h_1^B(E^B)))} = \frac{h_1^B(E^B)}{h_1^C(f_{11}^{B \rightarrow C}(E^B))} = \frac{h_1^B(E^B)}{h_1^C(E^C)}. \tag{24}$$

Moreover, if instead of B and C we consider systems R and B and we write the definition of temperature according to Eq. (18) and use Eq. (24), we obtain

$$\frac{T_1^B}{T_1^R} = \left. \frac{d f_{11}^{R \rightarrow B}(E^R)}{dE^R} \right|_{E_1^R} = \frac{h_1^R(E_1^R)}{h_1^B(f_{11}^{R \rightarrow B}(E_1^R))} = \frac{h_1^R(E_1^R)}{h_1^B(E_1^B)} = \frac{k\beta^R(E_1^R)}{k\beta^B(E_1^B)} \tag{25}$$

in agreement with the usual QSM identification $\beta(E_1) = 1/kT_1$ for the temperature of the stable equilibrium state with energy E_1 . From the continuity of $\beta(E)$, it follows that also our Assumption 3 below is in agreement within QSM.

Inserting the relation $dS_{\text{vN,se}}(E)/dE = k\beta(E)$ and the identification $\beta(E) = 1/kT(E)$ in the integral calculus identity $\int_{E_1}^{E_2} \frac{dS_{\text{vN,se}}(E)}{dE} dE = S_{\text{vN,se}}(E_2) - S_{\text{vN,se}}(E_1)$, one obtains the relation $\int_{E_1}^{E_2} \frac{1}{T(E)} dE = S_{\text{vN,se}}(E_2) - S_{\text{vN,se}}(E_1)$ which substituted into our new definition of entropy below, Eq. (40), yields

$$S_1^A = S_0^A - \left[S_{\text{vN,se}}^B \left(E_{\text{se2rev}}^B \Big|_{A_0 A_1}^{\text{sw}, B_{\text{se1}}} \right) - S_{\text{vN,se}}^B (E_{\text{se1}}^B) \right]. \quad (26)$$

This relation, together with the additivity property of the von Neumann entropy functional and its invariance in unitary processes, essentially implies that our operational definition of entropy is fully compatible with the von Neumann entropy.

Corollary 3. The temperature of the stable equilibrium states of any system B is a function of its energy E^B and the region of space \mathbf{R}^B it occupies, i.e.,

$$T^B = T^B(E^B; \mathbf{R}^B), \quad (27)$$

provided the reference state R_{se1} of the reference system R and the arbitrary multiplicative constant T_{se1}^R that are necessary for the definition of T^B according to Eq. (18) have been chosen once and for all. The proof is in Footnote 11.

Remark. Choice of reference system and reference stable equilibrium state. In the macroscopic domain, the following choice of R and of R_{se1} is currently employed, because it can be easily reproduced in any laboratory. The reference system R is composed of a sufficient number of moles of pure water and its reference stable equilibrium state R_{se1} is any of the stable equilibrium states of R in which ice, liquid water, and water vapor coexist. This choice is convenient because, up to the measurement accuracy available today, the value of the limit in Eq. (18) is practically independent of both the number of moles in system R and the particular choice of the reference state R_{se1} , as long as it belongs to the set of triple-point states. With this selection for the reference stable equilibrium state, we obtain the S.I. thermodynamic temperature, with unit called *kelvin*, by setting $T_{\text{se1}}^R = 273.16$ K. In the microscopic field, it could be convenient to choose as a reference system R^μ a few-particle monoatomic gas and as a reference state of R^μ the stable equilibrium state R_{se1}^μ which according to the standard model in quantum statistical mechanics has a temperature $T_{\text{se1}}^{R^\mu} = 273.16$ K. Note that, by the next theorem (Theorem 4), we prove that the ratio of two temperatures can be measured directly and is independent of the choice of the reference system and of the reference stable equilibrium state. Hence, any system in any stable equilibrium state such that the temperature of the system is known can be used as a new reference system in a reference stable equilibrium state, without inconsistencies.

¹¹**Proof of Corollary 3.** The conclusion is a direct consequence of Postulate 2, Lemma 1 and definition (18). \square

Theorem 4. Let B_{se1} be any stable equilibrium state of a system B and let C_{se1} be any stable equilibrium state of a system C , both with a non vanishing temperature. Then, the ratio of the temperatures of B_{se1} and C_{se1} , as defined via Eq. (18), is independent of the choice of the reference system R and of the reference stable equilibrium state R_{se1} , and can be measured directly by the following procedure.

Consider the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$, where $\Pi_{XBrev}^{B_{se1}}$ is any reversible weight processes for XB standard with respect B and with initial state B_{se1} , $\Pi_{XCrev}^{C_{se1}}$ is any reversible weight processes for XC standard with respect C , with initial state C_{se1} and with the same initial and final state of X as $\Pi_{XBrev}^{B_{se1}}$, and X is a system which can be chosen and changed arbitrarily, as well as the initial state of X . On account of Lemma 2 the set of pairs of processes $\{(\Pi_{XBrev}^{B_{se1}}; \Pi_{XCrev}^{C_{se1}})\}$ defines a single valued and invertible function $f_{11}^{B \rightarrow C}(E^B)$, which is differentiable in E_{se1}^B . The ratio of the temperatures T_{se1}^C and T_{se1}^B is given by

$$\frac{T_{se1}^C}{T_{se1}^B} = \lim_{E^B \rightarrow E_{se1}^B} \frac{f_{11}^{B \rightarrow C}(E^B) - f_{11}^{B \rightarrow C}(E_{se1}^B)}{E^B - E_{se1}^B} = \left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B}. \tag{28}$$

The proof is in Footnote 12. Theorem 4 completes the definition of temperature of a stable equilibrium state.

6. Definition of thermodynamic entropy for any state

Corollary 4. Consider a pair of stable equilibrium states (B_{se1}, C_{se1}) and the set of processes which defines the function $E^C = f_{11}^{B \rightarrow C}(E^B)$ according to Lemma 2. Then, for every pair of stable equilibrium states of B and C determined by the same regions of space \mathbf{R}^B and \mathbf{R}^C as B_{se1} and C_{se1} , respectively, and by the energy values E^B and $E^C = f_{11}^{B \rightarrow C}(E^B)$,

$$\frac{T^C(E^C = f_{11}^{B \rightarrow C}(E^B); \mathbf{R}^C)}{T^B(E^B; \mathbf{R}^B)} = \left. \frac{df_{11}^{B \rightarrow C}(E^B)}{dE^B} \right|_{E^B}. \tag{32}$$

The proof is in Footnote 13.

¹²**Proof of Theorem 4.** By applying to Eq. (10) the theorem on the derivative of a composite function, one obtains

$$\left. \frac{df_{11}^{B \rightarrow C}}{dE^B} \right|_{E_{se1}^B} = \left. \frac{df_{11}^{R \rightarrow C}}{dE^R} \right|_{E^R = f_{11}^{B \rightarrow R}(E_{se1}^B)} \left. \frac{df_{11}^{B \rightarrow R}}{dE^B} \right|_{E_{se1}^B}. \tag{29}$$

On account of Eq. (18), the first derivative at the right hand side of Eq. (29) can be rewritten as

$$\left. \frac{df_{11}^{R \rightarrow C}}{dE^R} \right|_{E_{se1}^R} = \frac{T_{se1}^C}{T_{se1}^R}. \tag{30}$$

By applying Eqs. (17) and (18), the second derivative at the right hand side of Eq. (29) can be rewritten as

$$\left. \frac{df_{11}^{B \rightarrow R}}{dE^B} \right|_{E_{se1}^B} = \frac{1}{\left. \frac{df_{11}^{R \rightarrow B}}{dE^R} \right|_{E_{se1}^R}} = \frac{1}{\frac{T_{se1}^B}{T_{se1}^R}} = \frac{T_{se1}^R}{T_{se1}^B}. \tag{31}$$

By combining Eqs. (29), (30) and (31) we obtain Eq. (28). □

¹³**Proof of Corollary 4.** For the fixed regions of space \mathbf{R}^B , consider the set of stable equilibrium states of system B defined by varying the energy E^B . Select a value of energy E^B and denote the corresponding state in this set by B_{se2} , i.e., $E_{se2}^B = E^B$. Consider the pair of stable equilibrium states (B_{se2}, C_{se2}) , where C_{se2} is such that

Assumption 3. For every system B and every choice of the regions of space \mathbf{R}^B occupied by the constituents of B , the temperature of the stable equilibrium states of B is a continuous function of the energy of B and is vanishing only in the stable equilibrium state with the lowest energy for the given regions of space \mathbf{R}^B .

Lemma 5. For every pair of stable equilibrium states B_{se1} and B_{se2} of a system B , with a non vanishing temperature and with the same regions of space \mathbf{R}^B occupied by the constituents of B , the integral

$$\int_{E_{se1}^B}^{E_{se2}^B} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B, \tag{34}$$

has a finite value and the same sign as $E_{se2}^B - E_{se1}^B$. The proof is in Footnote 14.

Theorem 5. Consider an arbitrarily chosen pair of states (A_1, A_2) of a system A , such that A is separable and uncorrelated from its environment, another system B in the environment of A and a reversible weight process $\Pi_{ABrev}^{B_{se1}}$ for AB in which A goes from A_1 to A_2 , standard with respect to B and with initial state B_{se1} , chosen so that the temperature of B is non vanishing both for B_{se1} and for the final state B_{se2} . Denote by \mathbf{R}^B the regions of space occupied by the constituents of B in its end states B_{se1} and B_{se2} . Then the value of the integral

$$\int_{E_{se1}^B}^{E_{se2rev}^B} \Big|_{A_1 A_2}^{sw, B_{se1}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B, \tag{35}$$

depends only on the pair of states (A_1, A_2) of system A and is independent of the choice of system B , of the initial stable equilibrium state B_{se1} , and of the details of the reversible weight process for AB , standard with respect to B . The proof is in Footnote 15.

$E_{se2}^C = f_{11}^{B \rightarrow C}(E_{se2}^B)$ and let $E^C = f_{22}^{B \rightarrow C}(E^B)$ be the function defined according to Lemma 2. Then, we have

$$\frac{T^C(E_{se2}^C; \mathbf{R}^C)}{T^B(E_{se2}^B; \mathbf{R}^B)} = \frac{T_{se2}^C}{T_{se2}^B} = \frac{df_{22}^{B \rightarrow C}(E^B)}{dE^B} \Big|_{E_{se2}^B} = \frac{df_{11}^{B \rightarrow C}(E^B)}{dE^B} \Big|_{E_{se2}^B}, \tag{33}$$

where the first equality obtains from Eq. (27), the second from Eq. (28) applied to $f_{22}^{B \rightarrow C}(E^B)$, and the third from Eq. (7). Recalling that $E_{se2}^B = E^B$, that E^B can be varied arbitrarily, and that $E_{se2}^C = f_{11}^{B \rightarrow C}(E^B)$, Eq. (33) yields Eq. (32). \square

¹⁴**Proof of Lemma 5.** Since both E_{se1}^B and E_{se2}^B are greater than the lowest energy value for the given regions of space \mathbf{R}^B , on account of Assumption 3 the function $1/T^B(E^B; \mathbf{R}^B)$ is defined and continuous in the whole interval. Therefore the integral in Eq. (34) exists. Moreover, on account of Corollary 1, the function $1/T^A(E; \mathbf{R}^A)$ has positive values. Therefore, if $E_{se2}^A > E_{se1}^A$ the integral in Eq. (34) has a positive value; if $E_{se2}^A < E_{se1}^A$ the integral in Eq. (34) has a negative value. \square

¹⁵**Proof of Theorem 5.** On account of Theorem 2, once the initial state B_{se1} has been chosen, the final state B_{se2} is determined uniquely. Therefore, the value of the integral in Eq. (35) can depend, at most, on the pair of states (A_1, A_2) and on the choice of system B and of its initial state B_{se1} . Consider another system C and a reversible weight process $\Pi_{ACrev}^{C_{se1}}$ for AC in which A goes again from A_1 to A_2 , standard with respect to C and with an initial state C_{se1} chosen arbitrarily, provided that the temperature of C is non vanishing both for C_{se1} and for the final state C_{se2} . We will prove that the integral

$$\int_{E_{se1}^C}^{E_{se2rev}^C} \Big|_{A_1 A_2}^{sw, C_{se1}} \frac{1}{T^C(E^C; \mathbf{R}^C)} dE^C \tag{36}$$

Definition. Definition of thermodynamic entropy. Let (A_1, A_2) be any pair of states of a system A , such that A is separable and uncorrelated from its environment, and let B be any other system placed in the environment of A . We call *entropy difference* between A_2 and A_1 the quantity

$$S_2^A - S_1^A = - \int_{E_{se1}^B}^{E_{se2rev}^B} \Big|_{A_1 A_2}^{sw, B_{se1}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B, \tag{39}$$

where B_{se1} and B_{se2rev} are the initial and the final state of B in any reversible weight process for AB from A_1 to A_2 , standard with respect to B , \mathbf{R}^B is the set of regions of space occupied by the constituents of B in the states B_{se1} and B_{se2rev} , and T^B is the temperature of B . The initial state B_{se1} is chosen so that both T_{se1}^B and T_{se2rev}^B are non vanishing. On account of Theorem 5, the right hand side of Eq. (39) is determined uniquely by states A_1 and A_2 .

Let A_0 be a reference state of A , to which we assign an arbitrarily chosen value of entropy S_0^A . Then, the value of the entropy of A in any other state A_1 of A such that A is separable and uncorrelated from its environment is determined uniquely by the equation

$$S_1^A = S_0^A - \int_{E_{se1}^B}^{E_{se2rev}^B} \Big|_{A_0 A_1}^{sw, B_{se1}} \frac{1}{T^B(E; \mathbf{R}^B)} dE^B, \tag{40}$$

where B_{se1} and B_{se2rev} are the initial and the final state of B in any reversible weight process for AB from A_0 to A_1 , standard with respect to B , T_{se1}^B and T_{se2rev}^B are non vanishing, and the other symbols have the same meaning as in Eq. (39). Such a process exists for every state A_1 such that A is separable and uncorrelated from its environment, in a set of states where Assumption 1 holds.

Lemma 6. Let (A_1, A_2) be any pair of states of a system A such that A is separable and uncorrelated from its environment, and let B be any other system placed in the environment of A . Let Π_{ABirr} be any irreversible weight process for AB , standard with respect to B , from

has the same value as the integral in Eq. (35), implying that such value is independent of the choice of system B and of the initial state B_{se1} , and, therefore, it depends only on the pair of states (A_1, A_2) .

The set of pairs of processes $\{(\Pi_{ABrev}^{B_{se1}}, \Pi_{ACrev}^{C_{se1}})\}$ such that the energy of the final state of B is in the range $E_{se1}^B \leq E^B \leq E_{se2}^B$ belongs to the set defined in Lemma 2, so that $E^C = f_{11}^{B \rightarrow C}(E^B)$ and, since this function is invertible (Lemma 2), $E^B = f_{11}^{C \rightarrow B}(E^C)$ so that, in particular, $E_{se1}^B = f_{11}^{C \rightarrow B}(E_{se1}^C)$ and $E_{se2rev}^B \Big|_{A_1 A_2}^{sw, B_{se1}} = f_{11}^{C \rightarrow B}(E_{se2rev}^C \Big|_{A_1 A_2}^{sw, C_{se1}})$. Now, consider the change of integration variable in the definite integral (36) from $E^C = f_{11}^{B \rightarrow C}(E^B)$ to E^B . By virtue of Eq. (32) (Corollary 4) we have

$$dE^C = \frac{df_{11}^{B \rightarrow C}(E^B)}{dE^B} dE^B = \frac{T^C(f_{11}^{B \rightarrow C}(E^B); \mathbf{R}^C)}{T^B(E^B; \mathbf{R}^B)} dE^B. \tag{37}$$

Thus, the integral in Eq. (36) can be rewritten as follows

$$\begin{aligned} & \int_{f_{11}^{C \rightarrow B}(E_{se1}^C)}^{f_{11}^{C \rightarrow B}(E_{se2rev}^C \Big|_{A_1 A_2}^{sw, C_{se1}})} \frac{1}{T^C(f_{11}^{B \rightarrow C}(E^B); \mathbf{R}^C)} \frac{T^C(f_{11}^{B \rightarrow C}(E^B); \mathbf{R}^C)}{T^B(E^B; \mathbf{R}^B)} dE^B \\ &= \int_{E_{se1}^B}^{E_{se2rev}^B \Big|_{A_1 A_2}^{sw, B_{se1}}} \frac{1}{T^B(E; \mathbf{R}^B)} dE^B \end{aligned} \tag{38}$$

□

A_1 to A_2 , and let $B_{\text{se}1}$ and $B_{\text{se}2\text{irr}}$ be the end states of B in the process. Then

$$-\int_{E_{\text{se}1}^B}^{E_{\text{se}2\text{irr}}^B} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B < S_2^A - S_1^A . \quad (41)$$

The proof is in Footnote 16.

Remark. Approximate measurement of the entropy difference. A conceptually different but practically important issue is that, even within the domain of validity of Assumption 1 in a given nonequilibrium framework, the reversible weight processes for AB , standard with respect to B , that are assumed to be conceivable, may nevertheless be difficult or practically impossible to implement, whereas it may be easier to approximate them irreversibly. Consider a closed system A and a system B in its environment that fulfill Assumption 1 for the pair of states (A_1, A_2) of A and state $B_{\text{se}1}$ of B , as well as for the pair of states (A_2, A_1) of A and state $B_{\text{se}1'}$ of B . Assume that for both pairs we can perform an irreversible process under the conditions of Lemma 6. In such cases, of course, system B ends in different states than if the process were reversible: we denote the energies of the end states of B by $E_{\text{se}2\text{irr}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}}$ and $E_{\text{se}2'\text{irr}}^B|_{A_2A_1}^{\text{sw},B_{\text{se}1'}}$, respectively. Then, applying Lemma 6 to the two processes we obtain

$$-\int_{E_{\text{se}1}^B}^{E_{\text{se}2\text{irr}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B < S_2^A - S_1^A < \int_{E_{\text{se}1'}^B}^{E_{\text{se}2'\text{irr}}^B|_{A_2A_1}^{\text{sw},B_{\text{se}1'}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B . \quad (44)$$

Equation 44 allows one to establish experimentally, by performing two irreversible processes (protocols), an upper and a lower bound to the value of the entropy difference $S_2^A - S_1^A$. By repeated experiments it is thus possible to restrict the range between lower and upper bound so as to converge towards an acceptable degree of approximation.

7. Principle of entropy non-decrease, additivity of entropy, maximum entropy principle

Based on the above construction, in this section we obtain some of the main standard theorems about entropy and entropy change.

Theorem 6. Principle of entropy non-decrease in weight processes. Let (A_1, A_2) be a pair of states of a system A such that A is separable and uncorrelated from its environment and let $A_1 \xrightarrow{W} A_2$ be any weight process for A from A_1 to A_2 . Then, the entropy difference

¹⁶**Proof of Lemma 6.** Let $\Pi_{AB\text{rev}}$ be any reversible weight process for AB , standard with respect to B , from A_1 to A_2 , with the same initial state $B_{\text{se}1}$ of B , and let $B_{\text{se}2\text{rev}}$ be the final state of B in this process. On account of Theorem 2,

$$E_{\text{se}2\text{rev}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}} < E_{\text{se}2\text{irr}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}} . \quad (42)$$

Since T^B is a positive function, from Eqs. (42) and (39) one obtains

$$-\int_{E_{\text{se}1}^B}^{E_{\text{se}2\text{irr}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B < -\int_{E_{\text{se}1}^B}^{E_{\text{se}2\text{rev}}^B|_{A_1A_2}^{\text{sw},B_{\text{se}1}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B = S_2^A - S_1^A . \quad (43)$$

□

$S_2^A - S_1^A$ is equal to zero if and only if the weight process is reversible; it is strictly positive if and only if the weight process is irreversible. The proof is in Footnote 17.

Theorem 7. Additivity of entropy differences. Consider the pair of states ($C_1 = A_1B_1, C_2 = A_2B_2$) of the composite system $C = AB$, such that A, B and C are separable and uncorrelated from their environment. Then,

$$S_{2,2}^{AB} - S_{1,1}^{AB} = S_2^A - S_1^A + S_2^B - S_1^B . \tag{47}$$

The proof is in Footnote 18.

Remark. As a consequence of Theorem 7, if the values of entropy are chosen so that they are additive in the reference states, entropy results as an additive property.

¹⁷**Proof of Theorem 6.** If $A_1 \xrightarrow{w} A_2$ is reversible, then it is a special case of a reversible weight process for AB , standard with respect to B , in which the initial stable equilibrium state of B does not change. Therefore, $E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}} = E_{se1}^B$ and Eq. (39) yields

$$S_2^A - S_1^A = - \int_{E_{se1}^B}^{E_{se2rev}^B |_{A_1A_2}^{sw, B_{se1}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B = 0 . \tag{45}$$

If $A_1 \xrightarrow{w} A_2$ is irreversible, then it is a special case of an irreversible weight process for AB , standard with respect to B , in which the initial stable equilibrium state of B does not change. Therefore, $E_{se2irr}^B |_{A_1A_2}^{sw, B_{se1}} = E_{se1}^B$ and Eq. (41) yields

$$S_2^A - S_1^A > - \int_{E_{se1}^B}^{E_{se2irr}^B |_{A_1A_2}^{sw, B_{se1}}} \frac{1}{T^B(E^B; \mathbf{R}^B)} dE^B = 0 . \tag{46}$$

Moreover, if a weight process $A_1 \xrightarrow{w} A_2$ for A is such that $S_2^A - S_1^A = 0$, then the process must be reversible, because we just proved that for any irreversible weight process $S_2^A - S_1^A > 0$; if a weight process $A_1 \xrightarrow{w} A_2$ for A is such that $S_2^A - S_1^A > 0$, then the process must be irreversible, because we just proved that for any reversible weight process $S_2^A - S_1^A = 0$. \square

¹⁸**Proof of Theorem 7.** Let us choose a system D (with fixed regions of space \mathbf{R}^D) in the environment of C , and consider the processes $\Pi_{ADrev} = A_1D_{se1} \xrightarrow{wrev} A_2D_{se3rev}$ and $\Pi_{BDrev} = B_1D_{se3rev} \xrightarrow{wrev} B_2D_{se2rev}$. For process Π_{ADrev} Eq. (39) implies that

$$S_2^A - S_1^A = - \int_{E_{se1}^D}^{E_{se3rev}^D |_{A_1A_2}^{sw, D_{se1}}} \frac{1}{T^D(E^D; \mathbf{R}^D)} dE^D . \tag{48}$$

For process Π_{BDrev} Eq. (39) implies that

$$S_2^B - S_1^B = - \int_{E_{se3rev}^D |_{A_1A_2}^{sw, D_{se1}}}^{E_{se2rev}^D |_{B_1B_2}^{sw, D_{se3rev}}} \frac{1}{T^D(E^D; \mathbf{R}^D)} dE^D . \tag{49}$$

The composite process $(\Pi_{ADrev}, \Pi_{BDrev}) = A_1B_1D_{se1} \xrightarrow{wrev} A_2B_1D_{se3rev} \xrightarrow{wrev} A_2B_2D_{se2rev}$ is a reversible weight process from $C_1 = A_1B_1$ to $C_2 = A_2B_2$ for CD , standard with respect to D , in which the energy change of D is the sum of its energy changes in the constituent processes Π_{ADrev} and Π_{BDrev} . Therefore, Eq. (39) implies that

$$S_2^C - S_1^C = - \int_{E_{se1}^D}^{E_{se2rev}^D |_{C_1C_2}^{sw, D_{se1}} = E_{se3rev}^D |_{A_1A_2}^{sw, D_{se1}} + E_{se2rev}^D |_{B_1B_2}^{sw, D_{se3rev}}} \frac{1}{T^D(E^D; \mathbf{R}^D)} dE^D . \tag{50}$$

Subtracting Eqs. (48) and (49) from Eq. (50) yields Eq. (47). \square

Theorem 8. Maximum entropy principle. Consider a closed system A , and the set of all the states of A with a given value E_1^A of the energy, given regions of space \mathbf{R}^A , and such that A is separable and uncorrelated from its environment. Then, the entropy of A has the highest value in this set of states only in the unique stable equilibrium state $A_{\text{se1}} = A_{\text{se}}(E_1^A; \mathbf{R}^A)$ determined by \mathbf{R}^A and the value E_1^A . The proof is in Footnote 19.

8. Definition of entropy extended to sets of states that do not fulfill Assumption 1

In this section we extend our operational definition of thermodynamic entropy to a broader class of system models for which Assumption 1 is fulfilled only within one or more subsets of states. We begin by relaxing Assumption 1 as follows.

Relaxed Assumption 1. Any given state A_1 of any closed system A such that A is separable and uncorrelated from its environment, either belongs to a set Σ_A where every pair of states fulfills Assumption 1 or it can be reached from at least one state of Σ_A by means of a weight process for A and it can be the initial state of at least one weight process for A having as final state a state of Σ_A .

Definition. Definition of thermodynamic entropy. For the states in Σ_A we adopt the definition given in Section 6. For every state A_1 that does not belong to Σ_A , we associate a range of entropy values, as follows. Let $A_{1\text{low}}$ be the state with highest entropy, in Σ_A , such that a weight process for A from $A_{1\text{low}}$ to A_1 is possible, and let $A_{1\text{high}}$ be the state with lowest entropy, in Σ_A , such that a weight process for A from $A_{1\text{high}}$ to A_1 is possible. The existence of such states is granted by Relaxed Assumption 1. Then the range of entropy values associated with state A_1 is

$$S_{1\text{low}}^A \leq S_1^A \leq S_{1\text{high}}^A . \quad (51)$$

Theorem 9. Principle of entropy non-decrease in weight processes. Let A_1 and A_2 be two states of system A , such that all the entropy values in the range associated with A_2 are higher than all the entropy values in the range associated with A_1 , namely, $S_{2\text{low}}^A > S_{1\text{high}}^A$. Then a weight process for A from A_2 to A_1 is impossible. The proof is in Footnote 20.

Theorem 10. Additivity of entropy. Consider a state $(AB)_1 = A_1 B_1$ of a composite system AB fulfilling Relaxed Assumption 1 and such that A and B are separable and uncorrelated. Denote by $\left[S_{1\text{low}}^A, S_{1\text{high}}^A \right]$ the range of entropy values associated with state A_1 , and with

¹⁹**Proof of Theorem 8.** Let A_1 be any state different from A_{se1} in the set of states of A considered here. On account of Postulate 3 a zero work weight process $A_1 \xrightarrow{w} A_{\text{se1}}$ exists and is irreversible because a zero work weight process $A_{\text{se1}} \xrightarrow{w} A_1$ would violate the definition of stable equilibrium state. Therefore, Lemma 6 implies $S_{\text{se1}}^A > S_1^A$. \square

²⁰**Proof of Theorem 9.** Weight processes $A_{2\text{low}} \xrightarrow{w} A_2$ and $A_1 \xrightarrow{w} A_{1\text{high}}$ exist by definition of $A_{2\text{low}}$ and of $A_{1\text{high}}$. Suppose that, contrary to the conclusion, a weight process $A_2 \xrightarrow{w} A_1$ exists. Then, a weight process $A_{2\text{low}} \xrightarrow{w} A_2 \xrightarrow{w} A_1 \xrightarrow{w} A_{1\text{high}}$ would exist and, since $S_{2\text{low}}^A > S_{1\text{high}}^A$, would violate the principle of entropy nondecrease in Σ_A already proved in Theorem 6. \square

$\left[S_{1low}^B, S_{1high}^B \right]$ the range for state B_1 . If the entropy values in the reference states of A , B and AB have been chosen so that in Σ_{AB} the entropy of any state of AB in which A and B are separable and uncorrelated equals the sum of the entropy values of A and B , then the range of entropy values associated with state A_1B_1 is contained in the interval $\left[S_{1low}^A + S_{1low}^B, S_{1high}^A + S_{1high}^B \right]$. The proof is in Footnote 21.

9. Conclusions

We presented a rigorous and general logical construction of an operational definition of thermodynamic entropy which can be applied, *in principle*, even to non-equilibrium states of few-particle systems, provided they are separable and uncorrelated from their environment. The new logical construction provides an operational definition of entropy which requires neither the concept of *heat* nor that of *thermal reservoir*. Therefore, it removes: (1) the logical limitations that restrict *a priori* the traditional definitions of entropy to the equilibrium states of many-particle systems; and (2) the operational limitations that restrict *in practice* to many-particle systems our previous definitions of non-equilibrium entropy because they hinged on the notion of thermal reservoirs.

²¹**Proof of Theorem 10.** Let $(AB)_{1low}$ be the highest entropy state in Σ_{AB} such that a weight process for AB from $(AB)_{1low}$ to A_1B_1 is possible. A weight process for AB from state $A_{1low}B_{1low}$ to A_1B_1 is possible, because it can be obtained by two separate weight processes for A and B . Therefore, $S_{1low,1low}^{AB} \leq S_{1low}^{AB}$ or, using the additivity in $\Sigma_A \times \Sigma_B$,

$$S_{1low}^A + S_{1low}^B = S_{1low,1low}^{AB} \leq S_{1low}^{AB} \quad (52)$$

Similarly, let $(AB)_{1high}$ be the lowest entropy state in Σ_{AB} such that a weight process for AB from A_1B_1 to $(AB)_{1high}$ is possible. A weight process for AB from state $A_{1high}B_{1high}$ to A_1B_1 is possible, because it can be obtained by two separate weight processes for A and B . Thus, we have $S_{1high}^{AB} \leq S_{1high,1high}^{AB}$, i.e.,

$$S_{1high}^{AB} \leq S_{1high,1high}^{AB} = S_{1high}^A + S_{1high}^B \quad (53)$$

By definition, the entropy range associated with state $(AB)_1$ is

$$S_{1low}^{AB} \leq S_1^{AB} \leq S_{1high}^{AB} \quad (54)$$

Therefore, combining Eqs. (52), (53), (54) yields our conclusion

$$S_{1low}^A + S_{1low}^B = S_{1low,1low}^{AB} \leq S_{1low}^{AB} \leq S_1^{AB} \leq S_{1high}^{AB} \leq S_{1high,1high}^{AB} = S_{1high}^A + S_{1high}^B \quad (55)$$

□

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