REMOVING HEAT AND CONCEPTUAL LOOPS FROM THE DEFINITION OF ENTROPY

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ABSTRACT

A rigorous and general logical scheme is presented, which provides an operative non-statistical definition of entropy valid also in the nonequilibrium domain and free of the usual conceptual loops and unnecessary assumptions that restrict the traditional definition of entropy to the equilibrium domain. The scheme is based on carefully worded operative definitions for all the fundamental concepts employed, including those of system, state of a system, isolated system, separable system, systems uncorrelated form each other, environment of a system, process and reversible process. The treatment considers also systems with movable internal walls and/or semipermeable walls, with chemical reactions and and/or external force fields, and with small numbers of particles. The definition of entropy involves neither the concept of heat nor that of quasistatic process; it applies to both equilibrium and nonequilibrium states. Simple and rigorous proofs of the additivity of entropy and of the principle of entropy nondecrease complete the logical framework.

INTRODUCTION

As is well known, classical thermodynamics was developed during the 19th century, due to the pioneering contributions by Carnot, Mayer, Joule, Kelvin, Clausius, Maxwell and Gibbs. In 1897, Planck [1] stated the second law in the form that is still used in most textbooks and is called Kelvin-Planck's statement of the second law: it is impossible to construct an engine which, working in a cycle, produces no effect except the raising of a weight and the cooling of a heat reservoir. In 1908, Poincaré [2] presented a complete structure of classical thermodynamics. The basic approach of Poincaré thermodynamics is still used in several university textbooks, with very small changes. In

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this approach, the first law is stated as follows: in a cycle, the work done by a system is proportional to the heat received by the system. In symbols, for a cycle:

$$Q = JW \quad , \tag{1}$$

where J is a universal constant which depends only on the system of units. From Eq. (1) it is easily deduced that, in a process of a system A from the initial state A_1 to the final state A_2, the quantity $JQ - W$ depends only on the states A_1 and A_2. Then, one defines the energy difference between A_2 and A_1 as the value of $JQ - W$ for A in the process, i.e.,

$$E_2^A - E_1^A = (JQ - W)_{12}^A \quad . \tag{2}$$

Clearly, Eq. (2) is vitiated by a logical circularity, because it is impossible to define heat without a previous definition of energy. The circularity of Eq. (2) was understood and resolved in 1909 by Carathéodory [3], who defined an adiabatic process without employing the concept of heat and stated the first law as follows: the work performed by a system in any adiabatic process depends only on the end states of the system. So, the first conceptual loop in classical thermodynamics, namely the use of the concept of heat in the definition of energy, was removed. Carathéodory proposed also a new statement of the second law, (in terms of adiabatic accessibility) which, however, is now used only in a few axiomatic treatments.

In 1937 Fermi [4] presented a well known treatment of classical thermodynamics. In this treatment, Carathéodory's statement of the first law is employed and rigorous theorems are used to define the thermodynamic temperature of a heat source and the entropy of a system. However, some unsatisfactory aspects still remain: the unnecessary concept of empirical temperature is used; the concepts of heat and of heat source are not defined rigorously; a reversible process is defined as a sequence of stable equilibrium states, *i.e.*, as a quasistatic process. Moreover, an incompleteness is present in the definition of the thermodynamic temperature of a heat source. Indeed, the definition is based on a theorem, in which Fermi considers a reversible cyclic engine which absorbs a quantity of heat Q_2 from a source at (empirical) temperature T_2 and supplies a quantity of heat Q_1 to a source at (empirical) temperature T_1. He states that if the engine performs n cycles, the quantity of heat subtracted from the first source is $n\,Q_2$ and the quantity of heat supplied to the second source is $n\,Q_1$. Thus, Fermi assumes implicitly that the quantity of heat exchanged in a cycle between a source and a reversible cyclic engine is independent of the initial state of the source. This incompleteness in the deductive scheme of thermodynamics is resolved only in the treatment presented here.

A few decades after Fermi's contribution, two schools of thermodynamics produced relevant further developments. The Prigogine school [5] studied the extension of the theory to non-equilibrium states and developed the thermodynamics of irreversible processes, pioneered in 1931 by Onsager [6]. The Keenan school deepened the conceptual foundations of thermodynamics and strengthened the bridge between quantum mechanics and thermodynamics. Some improvements of the logical foundations of thermodynamics due to the Keenan school are as follows.

Hatsopoulos and Keenan [7] analyzed deeply the meaning of the Kelvin-Planck statement of the second law. They pointed out that, with the term reservoir, Planck did not mean a system in either metastable or unstable equilibrium, but a system in stable equilibrium; otherwise, the statement of the second law would be false. However, when a stable equilibrium state is defined rigorously, the Kelvin-Planck statement becomes a corollary of the definition. They called stable equilibrium a state from which a finite change of state of the system cannot occur without a corresponding finite permanent change of the state of the environment; then, they proved a generalized form of the Kelvin-Planck statement of the second law as a consequence of the definitions of stable equilibrium state and of normal system. Thus, they removed the second conceptual loop in classical thermodynamics, *i.e.* the circularity in the Kelvin-Planck statement.

Hatsopoulos and Keenan stated the second law as follows: A system having specified allowed states and an upper bound in volume can reach from any given state a stable state and leave no net effect on the environment [7, p.34, p.373]. They also removed from the logical framework of thermodynamics the use of the unnecessary concept of empirical temperature. Indeed, they showed that thermodynamic temperature can be defined directly, without a previous definition of empirical temperature. They also tried to remove the concept of heat from the definition of entropy. Indeed, they presented the definition of entropy in two ways: the first through the concept of heat (which they defined rigorously); the second without the concept of heat. The second definition, however, was incomplete, because according to it the entropy difference between two states of a system could be measured only by means of a standard thermal reservoir, chosen once and for all.

Gyftopoulos and Beretta [8] completed the definition of entropy outlined by Hatsopoulos and Keenan; they presented a treatment of thermodynamics in which the definition of entropy is not based on the concepts of heat and of quasistatic process, so that the definition applies, potentially, also to local nonequilibrium states. They also broadened and made more rigorous the set of the basic definitions on which the theory of thermodynamics is based.

The increasing interest in nonequilibrium thermodynamics, as well as the recent scientific revival of thermodynamics in quantum theory (quantum heat engines [9], quantum Maxwell demons [10], quantum erasers [11], etc.) and the recent quest for quantum mechanical explanations of irreversibility (see *e.g.* Ref. [12]), suggest the need for further improvements of the treatment presented in Ref. [8], in order to obtain a rigorous and general treatment of the foundations of thermodynamics which, by the simplest possible conceptual scheme, extends the definition of entropy to the nonequilibrium domains and, being compatible with the quantum formalism, is suitable for unambiguous fundamental discussions on second law implications, even in the framework of quantum theory.

In the present paper, Ref. [8] is assumed as a starting point and two further objectives are pursued. The basic definitions of system, state, isolated system, separable system, environment of a system and process are further deepened, by developing a logical scheme outlined in Ref. [9]. The operative and general definitions of these concepts as presented here are valid also in the presence of internal semipermeable walls and reaction mechanisms. Moreover, the treatment of Ref. [8] is, on one hand, simplified by identifying the minimal set of definitions, assumptions and theorems which yield the definition of entropy and the principle of entropy non-decrease in a more direct way. On the other hand, the definition of a reversible process is given with reference to the concept of scenario; the latter is the largest isolated system whose subsystems are available for interaction, for the class of processes under exam. In this way, the operativity of the definition is improved and the treatment becomes more explicitly compatible also with old [10] and recent [11] interpretations of entropy and irreversibility in the quantum theoretical framework.

BASIC DEFINITIONS

Constituents, amounts of constituents. We call *constituents* the material particles chosen to describe the matter contained in any region of space R, at a time instant t. Examples of constituents are: atoms, molecules, ions, protons, neutrons, electrons. Constituents may combine and/or transform into other constituents according to a set of model-specific *reaction mechanisms*. We call *amount of constituent* i in any region of space R, at a time instant t, the number of particles of constituent i contained in R, at time t.

Region of space which contains particles of the i-th **constituent**. We will call region of space which contains particles of the i-th constituent a connected region R_i of physical space (the three-dimensional Euclidean space) in which particles of the i-th constituent are contained. The boundary surface of R_i may be a patchwork of *walls*, i.e., surfaces impermeable to particles of the i-th constituent, and ideal surfaces (permeable to particles of the i-th constituent). The geometry and the permeability features of the boundary surface of R_i (walls, ideal surfaces) can vary in time, as well as the number of particles contained in R_i.

Collection of matter. We call *collection of matter*, denoted by C^A, a set of particles of one or more constituents which is described by specifying the allowed reaction mechanisms between different constituents and, at any time instant t, the set of r connected regions of space, $\boldsymbol{\mathsf{R}}^A = \mathsf{R}_1^A, \ldots, \mathsf{R}_i^A, \ldots, \mathsf{R}_r^A$, each of which contains n_i^A particles of a single kind of constituent. The regions of space $\boldsymbol{\mathsf{R}}^A$ can vary in time and overlap. Two regions of space may contain the same kind of constituent provided that they do not overlap. Thus, the *i-th* constituent could be identical with the *j-th* constituent, provided that R_i^A and R_j^A are disjoint.

Comment. This method allows a simple general description of the presence of internal walls and/or internal *semipermeable* membranes, *i.e.*, surfaces which can be crossed only by some kinds of con-

stituents and not others. An example of the method is illustrated in Figure 1: a collection of matter C^A with constituents O_2 and N_2, with a movable external wall and with two movable internal membranes, permeable to O_2 and to N_2 respectively, is represented by two overlapping regions of space, R_1^A and R_2^A, each bounded by a movable wall: R_1^A contains O_2, while R_2^A contains N_2.
In the simplest case of a collection of matter without internal partitions, the regions of space $\boldsymbol{R}^A$ coincide at every time instant.

Composition. We call *composition* of a collection of matter C^A, at a time instant t, the vector $\boldsymbol{n}^A$ with r components which specifies the number of particles contained at time t in each region of space R_i^A of C^A.

Compatible compositions, set of compatible compositions. We say that two compositions, $\boldsymbol{n}^{1A}$ and $\boldsymbol{n}^{2A}$ of a given collection of matter C^A are *compatible* if the change between $\boldsymbol{n}^{1A}$ and $\boldsymbol{n}^{2A}$ or viceversa can take place as a consequence of the allowed reaction mechanisms without matter exchange. We will call *set of compatible compositions* for a collection of matter C^A the set of all the compositions of C^A which are compatible with a given one, $\boldsymbol{n}^{0A}$. We will denote a set of compatible compositions by the symbol $(\boldsymbol{n}^{0A}, \boldsymbol{\nu}^A)$, where $\boldsymbol{\nu}^A$ is the matrix of the stoichiometric coefficients.

External force field. Let us denote by $\mathbf{F}$ a force field given by the superposition of the gravitational field $\mathbf{G}$, the electric field $\mathbf{E}$ and the magnetic field $\mathbf{H}$. Let us denote by Σ_t^A the union of the regions of space R_t^A in which the constituents of C^A are contained, at a time instant t, which will also be called region of space occupied by C^A at time t. Let us denote by Σ^A the union of all the regions of space Σ_t^A, *i.e.*, the whole region of space spanned by the matter and the walls of C^A, during the time evolution of C^A.
We call *external force field* for C^A at time t, denoted by $\mathbf{F}_{e,t}^A$, the spatial distribution of $\mathbf{F}$ which is measured at time t in Σ_t^A if all the constituents and the walls of C^A are removed and placed far away from Σ_t^A. We call *external force field* for C^A, denoted by $\mathbf{F}_e^A$, the spatial and time distribution of $\mathbf{F}$ which is measured in Σ^A if all the constituents and the walls of C^A are removed and placed far away from Σ^A.

System, properties of a system. We will call *system A* a collection of matter C^A defined by the initial composition $\boldsymbol{n}^{0A}$, the stoichiometric coefficients $\boldsymbol{\nu}^A$ of the allowed reaction mechanisms, and the possibly time-dependent specification, *over the entire time interval of interest*, of:

- the geometrical variables and the nature of the boundary surfaces that define the regions of space $\boldsymbol{R}_t^A$,
- the rates $\dot{\boldsymbol{n}}_t^{A\leftarrow}$ at which particles are transferred in or out of the regions of space, and
- the external force field distribution $\mathbf{F}_{e,t}^A$ for C^A,

provided that the following conditions apply:

1. an ensemble of identically prepared replicas of C^A can be obtained at any instant of time t, according to a specified set of instructions or preparation scheme;
2. a set of measurement procedures, $P_1^A, \dots, P_n^A$, exists, such that when each P_i^A is applied on replicas of C^A at any given instant of time t, the arithmetic mean $\langle P_i^A \rangle_t$ of the numerical outcomes of repeated applications of P_i^A is a value which is the same for every subensemble of replicas of C^A (the latter condition guarantees the so-called statistical *homogeneity* of the ensemble); $\langle P_i^A \rangle_t$ is called the *value of* P_i^A for C^A at time t;
3. the set of measurement procedures, $P_1^A, \dots, P_n^A$, is *complete* in the sense that the set of values $\{\langle P_1^A \rangle_t, \dots, \langle P_n^A \rangle_t\}$ allows to predict the value at time t of any other measurement procedure satisfying condition 2.

Then, each measurement procedure satisfying conditions 2 and 3 is called a *property* of system A, and the set $P_1^A, \dots, P_n^A$ a *complete set of properties* of system A.

State of a system. Given a system A as just defined, we call *state of system A at time t*, denoted by A_t, the set of the values *at time t* of

- all the properties of the system or, equivalently, of a complete set of properties, $\{\langle P_1 \rangle_t, \dots, \langle P_n \rangle_t\}$,
- the amounts of constituents, $\boldsymbol{n}_t^A$,
- the geometrical variables and the nature of the boundary surfaces of the regions of space $\boldsymbol{R}_t^A$,
- the rates $\dot{\boldsymbol{n}}_t^{A\leftarrow}$ of particle transfer in or out of the regions of space, and
- the external force field distribution in the region of space Σ_t^A occupied by A at time t, $\mathbf{F}_{e,t}^A$.

Closed system, open system. A system A is called a *closed system* if, at every time instant t, the boundary surface of every region of space R_{it}^A is a wall. Otherwise, A is called an *open system.*

Comment. For a closed system, in each region of space R_i^A, the number of particles of the i-th constituent can change only as a consequence of allowed reaction mechanisms.

Composite system, subsystems. If systems A and B, defined in the same time interval, are such that no region of space R_i^A overlaps with any region of space R_j^B, we will say that the system C whose regions of space of are $\boldsymbol{R}^C = R_1^A, \dots, R_i^A, \dots, R_{r_A}^A, R_1^B, \dots, R_j^B, \dots, R_{r_B}^B$ is the *composite* of systems A and B, and that A and B are *subsystems* of C. Then, we write $C = AB$ and denote its state at time t by $C_t = (AB)_t$.

Isolated system. We say that a closed system I is an isolated system in the stationary external force field $\mathbf{F}_e^I$, or simply an *isolated system*, if during the whole time evolution of I: (a)I is surrounded by a region of space in which no material particle is present, and (b) the external force field $\mathbf{F}_e^I$ is stationary, *i.e.*, time independent.

Separable closed systems. Consider a composite system AB, with A and B closed subsystems.

We say that systems A and B are *separable* at time t if, at that instant:

- the force field external to A coincides (where defined) with the force field external to AB, i.e., $\mathbf{F}_{e,t}^{A} = \mathbf{F}_{e,t}^{AB}$;
- the force field external to B coincides (where defined) with the force field external to AB, i.e. $\mathbf{F}_{e,t}^{B} = \mathbf{F}_{e,t}^{AB}$.

Comment. In simpler words, system A is separable from B at time t, if at that instant the force field produced by B is vanishing in the region of space occupied by A and viceversa. During the subsequent time evolution of AB, A and B need not remain separable at all times.

Systems uncorrelated from each other. Consider a composite system AB such that at time t the states A_t and B_t of the two subsystems fully determine the state $(AB)_t$, *i.e.*, the values of all the properties of AB can be determined by *local* measurements of properties of systems A and B. Then we say that systems A and B are *uncorrelated from each other* at time t, and we write the state of AB at time t as $(AB)_t = A_t B_t$.

Environment of a system, scenario. If a system A is a subsystem of an isolated system $I = AB$, we can choose AB as the isolated system to be studied. Then, we call B the *environment* of A, and we call AB the *scenario* under which A is studied.

Comment. The chosen scenario AB contains as subsystems all and only the systems that are allowed to interact with A; all the remaining systems in the universe are considered as not available for interaction.

Process, cycle. We call *process* for a system A from state A_1 to state A_2 in the scenario AB, denoted by $(AB)_1 \to (AB)_2$, the change of state from $(AB)_1$ to $(AB)_2$ of the isolated system AB which defines the scenario.

Restriction, for brevity. In the following (for brevity) we will consider only *closed systems* and only states of a closed system A in which A is separable and uncorrelated from its environment. Moreover, for a composite system AB, we will consider only states such that the subsystems A and B are separable and uncorrelated from each other.

Reversible process, reverse of a reversible process. A process for A in the scenario AB, $(AB)_1 \to (AB)_2$, is called a *reversible process* if there exists a process $(AB)_2 \to (AB)_1$ which restores the initial state of the isolated system AB. The process $(AB)_2 \to (AB)_1$ is called *reverse* of process $(AB)_1 \to (AB)_2$.

Comment. A reversible process need not be slow. In the general framework we are setting up, it is noteworthy that nowhere we state nor we need the concept that a process to be reversible needs to be *slow* in some sense.

Weight. We call *weight* a system M always separable and uncorrelated from its environment, such that:

- M is closed, it has a single constituent, with fixed number of particles and mass m, contained in a single region of space whose shape and volume are fixed;
- in any process, the difference between the initial and the final state of M is determined uniquely by the change in the position z of the center of mass of M, which can move only along a straight line whose direction coincides with that of a uniform and stationary external gravitational force field $\mathbf{G}_e = -g\mathbf{k}$, where g is a constant gravitational acceleration.

Weight process, work in a weight process. A process of a system A is called a *weight process*, denoted by $(A_1 \to A_2)_W$, if the only effect external to A is the displacement of the center of mass of a weight M between two positions z_1 and z_2 (see sketch in Figure 2). We call *work performed by A in the weight process*, denoted by the symbol $W_{12}^{A\to}$, the quantity

$$W_{12}^{A\to} = mg(z_2 - z_1) \ . \tag{3}$$

We will say that the work is *done* by A if $z_2 > z_1$ or is *received* by A if $z_2 < z_1$. Two equivalent symbols for the opposite of this work are $-W_{12}^{A\to} = W_{12}^{A\leftarrow}$.

Equilibrium state of a closed system. A state A_t of a system A, with environment B, is called an *equilibrium state* if:

- state A_t does not change with time;
- state A_t can be reproduced while A is an isolated system in the external force field $\mathbf{F}_e^A$, which coincides with $\mathbf{F}_e^{AB}$.

Stable equilibrium state of a closed system. An equilibrium state of a closed system A is called a *stable equilibrium state* if it cannot be modified in any process such that neither the geometrical configuration of the walls which bound the regions of space $\boldsymbol{R}^A$ nor the state of the environment B of A have net changes.

DEFINITION OF ENERGY FOR A CLOSED SYSTEM

First Law. Every pair of states (A_1, A_2) of a system A can be interconnected by means of a weight process for A. The works performed by the system in any two weight processes between the same initial and final states are identical.

Definition of energy for a closed system. Proof that it is a property. Let (A_1, A_2) be any pair of states of a system A. We call *energy difference* between states A_2 and A_1 either the work $W_{12}^{A\leftarrow}$ received by A in any weight process from A_1 to A_2 or the work $W_{21}^{A\to}$ done by A in any weight process from A_2 to A_1; in symbols:

$$E_2^A - E_1^A = W_{12}^{A\leftarrow} \quad \text{or} \quad E_2^A - E_1^A = W_{21}^{A\rightarrow}. \tag{4}$$

The first law guarantees that at least one of the weight processes considered in Eq. (4) exists. Moreover, it yields the following consequences:

(a) if both weight processes $(A_1 \to A_2)_W$ and $(A_2 \to A_1)_W$ exist, the two forms of Eq. (4) yield the same result ($W_{12}^{A\leftarrow} = W_{21}^{A\rightarrow}$);

(b) the energy difference between two states A_2 and A_1 depends only on the states A_1 and A_2;

(c) (*additivity of energy differences*) consider a pair of states A_1B_1 and A_2B_2 of a composite system AB; then

$$E_2^{AB} - E_1^{AB} = E_2^A - E_1^A + E_2^B - E_1^B \ \ ; \tag{5}$$

(d) (*energy is a property*) let A_0 be a reference state of a system A, 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 is determined uniquely by the equation

$$E_1^A = E_0^A + W_{01}^{A\leftarrow} \quad \text{or} \quad E_1^A = E_0^A + W_{10}^{A\rightarrow} \tag{6}$$

where $W_{01}^{A\leftarrow}$ or $W_{10}^{A\rightarrow}$ is the work in any weight process for A either from A_0 to A_1 or from A_1 to A_0. Rigorous proofs of these consequences can be found in Refs. [8, 12], and will not be repeated here.

DEFINITION OF ENTROPY FOR A CLOSED SYSTEM

Assumption 1: **restriction to normal systems**. We call *normal system* any system A that, starting from every state, can be changed to a non-equilibrium state with higher energy by means of a weight process for A in which the regions of space $\boldsymbol{R}^A$ occupied by the constituents of A have no net changes. From here on, we consider only normal systems.

Comment. In traditional treatments of thermodynamics, Assumption 1 is *not stated explicitly, but it is used*, for example when one states that any amount of work can be transferred to a thermal reservoir by a stirrer.

Theorem 1. Impossibility of a 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 $\boldsymbol{R}^A$ occupied by the constituents of A have no net change.

Proof. (See sketch in Figure 3) 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 $\boldsymbol{R}^A$ occupied by the constituents of A have no net change. On account of Assumption 1, it would be possible to perform a weight process Π_2 for A in which the regions of space $\boldsymbol{R}^A$ occupied by the constituents of 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 nonequilibrium state, namely, a state clearly different from A_{se}. Thus, the zero-work sequence of weight processes (Π_1, Π_2) would violate the definition of stable equilibrium state.

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

Lemma 1. Uniqueness of the stable equilibrium state. There can be no pair of different stable equilibrium states of a closed system A with identical regions of space $\boldsymbol{R}^A$ and the same value of the energy E^A.

Proof. Since A is closed and in any stable equilibrium state it is separable and uncorrelated from its environment, if two such states existed, by the first law and the definition of energy they could be interconnected by means of a zero-work weight process. So, at least one of them could be changed to a different state with no external effect, and hence would not satisfy the definition of stable equilibrium state.

Comment. Recall that for a closed system, the composition $\boldsymbol{n}^A$ belongs to the set of compatible compositions $(\boldsymbol{n}^{0A}, \boldsymbol{\nu}^A)$ fixed once and for all by the definition of the system.

Lemma 2. Any stable equilibrium state A_s of a system A is accessible via an irreversible zero-work weight process from any other state A_1 with the same regions of space $\boldsymbol{R}^A$ and the same value of the energy E^A.

Proof. By the first law and the definition of energy, A_s and A_1 can be interconnected by a zero-work weight process for A. However, a zero-work weight process from A_s to A_1 would violate the definition of stable equilibrium state. Therefore, the process must be in the direction from A_1 to A_s. The absence of a zero-work weight process in the opposite direction, implies that any zero-work weight process from A_1 to A_s is irreversible.

Systems in mutual stable equilibrium. We say that two systems A and B, each in a stable equilibrium state, are in mutual stable equilibrium if the composite system AB is in a stable equilibrium state.

Thermal reservoir. We call thermal reservoir a closed and always separable system R with a single constituent, contained in a fixed region of space, with a vanishing external force field, with energy values restricted to a finite range in which any pair of identical copies of the reservoir, R and R^d, is in mutual stable equilibrium when R and R^d are in stable equilibrium states.

Comment. Every single-constituent system without internal boundaries and applied external fields, and with a number of particles of the order of one mole (so that the *simple system* approximation as defined in Ref. [8, p.263] applies), when restricted to a fixed region of space of appropriate volume and to the range of energy values corresponding to the so-called *triple-point* stable equilibrium states, is a thermal reservoir.

Reference thermal reservoir. A thermal reservoir chosen once and for all, will be called a *reference thermal reservoir.* To fix ideas, we will choose water as the constituent of our reference thermal reservoir, *i.e.*, sufficient amounts of ice, liquid water, and water vapor at triple point conditions.

Standard weight process. Given a pair of states (A_1, A_2) of a system A and a thermal reservoir R, we call *standard weight process* for AR from A_1 to A_2 a weight process for the composite system AR in which the end states of R are stable equilibrium states. We denote by $(A_1R_1 \to A_2R_2)^{\rm sw}$ a standard weight process for AR from A_1 to A_2 and by $(\Delta E^R)^{\rm sw}_{A_1A_2}$ the corresponding energy change of the thermal reservoir R.

Assumption 2. Every pair of states $(A_1,\ A_2)$ of a system A can be interconnected by a reversible standard weight process for AR, where R is an arbitrarily chosen thermal reservoir.

Comment. Statements of the Second Law. The combination of Assumption 2 with the statement of the Second Law and Lemma 1 given above, forms our re-statement of the *Gyftopoulos-Beretta statement of the Second Law* [8, p. 62-63], which, in turn, is a restatement of that introduced by Hatsopoulos and Keenan [7, p.34, p.373]. The motivation for the separation in three parts of the statement proposed in Ref. [8] is as follows: to extract from the postulate a part which can be proved (Lemma 1); to separate *logically independent* assumptions, *i.e.*, assumptions such that a violation of the first would not imply a violation of the second, and *vice-versa*.

In addition to the Kelvin-Planck statement discussed above, also the well-known historical statements due to Clausius and to Carathéodory unfold as rigorous theorems in our logical scheme. Proofs can be found in Ref. [8, p.64, p.121, p.133].

Theorem 2. For a given system A and a given reservoir R, among all the standard weight processes for AR between a given pair of states $(A_1,\ A_2)$ of A, the energy change $(\Delta E^R)^{\rm sw}_{A_1A_2}$ of the thermal reservoir R has a lower bound which is reached if and only if the process is reversible.

Proof. Let Π_{AR} denote a standard weight process for AR from A_1 to A_2, and $\Pi_{AR\rm rev}$ a reversible one; the energy changes of R in processes Π_{AR} and $\Pi_{AR\rm rev}$ are, respectively, $(\Delta E^R)^{\rm sw}_{A_1A_2}$ and $(\Delta E^R)^{\rm swrev}_{A_1A_2}$. With the help of Figure 4, we will prove that, regardless of the initial state of R:
a) $(\Delta E^R)^{\rm swrev}_{A_1A_2} \le (\Delta E^R)^{\rm sw}_{A_1A_2}$;
b) if also Π_{AR} is reversible, then $(\Delta E^R)^{\rm swrev}_{A_1A_2} = (\Delta E^R)^{\rm sw}_{A_1A_2}$;
c) if $(\Delta E^R)^{\rm swrev}_{A_1A_2} = (\Delta E^R)^{\rm sw}_{A_1A_2}$, then also Π_{AR} is reversible.

Proof of a). Let us denote by R_1 and R_2 the initial and the final states of R in process $\Pi_{AR\text{rev}}$. Let us denote by R^d the duplicate of R which is employed in process Π_{AR}, and by R^d_3 and R^d_4 the initial and the final states of R^d in this process. Let us suppose, *ab absurdo*, that $(\Delta E^R)^{\text{swrev}}_{A_1A_2} > (\Delta E^R)^{\text{sw}}_{A_1A_2}$. Then, the sequence of processes $(-\Pi_{AR\text{rev}},\, \Pi_{AR})$ would be a weight process for RR^d in which, starting from the stable equilibrium state $R_2R^d_3$, the energy of RR^d is lowered and the regions of space occupied by the constituents of RR^d have no net changes, in contrast with Theorem 1. Therefore, $(\Delta E^R)^{\text{swrev}}_{A_1A_2} \leq (\Delta E^R)^{\text{sw}}_{A_1A_2}$.

Proof of b). If Π_{AR} is reversible too, then, in addition to $(\Delta E^R)^{\text{swrev}}_{A_1A_2} \leq (\Delta E^R)^{\text{sw}}_{A_1A_2}$, the relation $(\Delta E^R)^{\text{sw}}_{A_1A_2} \leq (\Delta E^R)^{\text{swrev}}_{A_1A_2}$ must hold too. Otherwise, the sequence of processes $(\Pi_{AR\text{rev}},\, -\Pi_{AR})$ would be a weight process for RR^d in which, starting from the stable equilibrium state $R_1R^d_4$, the energy of RR^d is lowered and the regions of space occupied by the constituents of RR^d have no net changes, in contrast with Theorem 1. Therefore, $(\Delta E^R)^{\text{swrev}}_{A_1A_2} = (\Delta E^R)^{\text{sw}}_{A_1A_2}$.

Proof of c). Let Π_{AR} be a standard weight process for AR, from A_1 to A_2, such that $(\Delta E^R)^{\text{sw}}_{A_1A_2} = (\Delta E^R)^{\text{swrev}}_{A_1A_2}$, and let R_1 be the initial state of R in this process. Let $\Pi_{AR\text{rev}}$ be a reversible standard weight process for AR, from A_1 to A_2, with the same initial state R_1 of R. Thus, R^d_3 coincides with R_1 and R^d_4 coincides with R_2. The sequence of processes $(\Pi_{AR},\, -\Pi_{AR\text{rev}})$ is a cycle for the isolated system ARB, where B is the environment of AR. As a consequence, Π_{AR} is reversible, because it is a part of a cycle of the isolated system ARB.

Theorem 3. Let R' and R'' be any two thermal reservoirs and consider the energy changes, $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}$ and $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$ respectively, in the reversible standard weight processes $\Pi_{AR'} = (A_1R'_1 \to A_2R'_2)^{\text{swrev}}$ and $\Pi_{AR''} = (A_1R''_1 \to A_2R''_2)^{\text{swrev}}$, where $(A_1,\, A_2)$ is an arbitrarily chosen pair of states of any system A. Then the ratio $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}/(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$:
a) is positive;
b) depends only on R' and R'', *i.e.*, it is independent of *(i)* the initial stable equilibrium states of R' and R'', *(ii)* the choice of system A, and *(iii)* the choice of states A_1 and A_2.

Proof of a). With the help of Figure 5, let us suppose that $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} < 0$. Then, $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$ cannot be zero. In fact, in that case the sequence of processes $(\Pi_{AR'},\, -\Pi_{AR''})$, which is a cycle for A, would be a weight process for R' in which, starting from the stable equilibrium state R'_1, the energy of R' is lowered and the regions of space occupied by the constituents of R' have no net changes, in contrast with Theorem 1. Moreover, $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$ cannot be positive. In fact, if it were positive, the work performed by $R'R''$ as a result of the overall weight process $(\Pi_{AR'},\, -\Pi_{AR''})$ for $R'R''$ would be

$$W^{R'R''\rightarrow} = -(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} + (\Delta E^{R''})^{\text{swrev}}_{A_1A_2} \ , \tag{7}$$

where both terms are positive. On account of Assumption 1 and Corollary 1, after the process $(\Pi_{AR'},\, -\Pi_{AR''})$, one could perform a weight process $\Pi_{R''}$ for R'' in which a positive amount of energy equal to $(\Delta E^{R''})^{\rm swrev}_{A_1A_2}$ is given back to R'' and the latter is restored to its initial stable equilibrium state. As a result, the sequence $(\Pi_{AR'},\ -\Pi_{AR''},\ \Pi_{R''})$ would be a weight process for R' in which, starting from the stable equilibrium state R'_1, the energy of R' is lowered and the regions of space occupied by the constituents of R' have no net changes, in contrast with Theorem 1. Therefore, the assumption $(\Delta E^{R'})^{\rm swrev}_{A_1A_2} < 0$ implies $(\Delta E^{R''})^{\rm swrev}_{A_1A_2} < 0$.

Let us suppose that $(\Delta E^{R'})^{\rm swrev}_{A_1A_2} > 0$. Then, for process $-\Pi_{AR'}$ one has $(\Delta E^{R'})^{\rm swrev}_{A_2A_1} < 0$. By repeating the previous argument, one proves that for process $-\Pi_{AR''}$ one has $(\Delta E^{R''})^{\rm swrev}_{A_2A_1} < 0$. Therefore, for process $\Pi_{AR''}$ one has $(\Delta E^{R''})^{\rm swrev}_{A_1A_2} > 0$.

Proof of b). Given a pair of states $(A_1,\ A_2)$ of a closed system A, consider the reversible standard weight process $\Pi_{AR'} = (A_1R'_1 \to A_2R'_2)^{\rm swrev}$ for AR', with R' initially in state R'_1, and the reversible standard weight process $\Pi_{AR''} = (A_1R''_1 \to A_2R''_2)^{\rm swrev}$ for AR'', with R'' initially in state R''_1. Moreover, given a pair of states $(A'_1,\ A'_2)$ of another closed system A', consider the reversible standard weight process $\Pi_{A'R'} = (A'_1R'_1 \to A'_2R'_3)^{\rm swrev}$ for $A'R'$, with R' initially in state R'_1, and the reversible standard weight process $\Pi_{A'R''} = (A'_1R''_1 \to A'_2R''_3)^{\rm swrev}$ for $A'R''$, with R'' initially in state R''_1.

With the help of Figure 6, we will prove that the changes in energy of the reservoirs in these processes obey the relation

$$\frac{(\Delta E^{R'})^{\rm swrev}_{A_1A_2}}{(\Delta E^{R''})^{\rm swrev}_{A_1A_2}} = \frac{(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2}}{(\Delta E^{R''})^{\rm swrev}_{A'_1A'_2}} \quad . \tag{8}$$

Let us assume: $(\Delta E^{R'})^{\rm swrev}_{A_1A_2} > 0$ and $(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2} > 0$, which implies, on account of part a) of the proof, $(\Delta E^{R''})^{\rm swrev}_{A_1A_2} > 0$ and $(\Delta E^{R''})^{\rm swrev}_{A'_1A'_2} > 0$. This is not a restriction, because it is possible to reverse the processes under exam. Now, as is well known, any real number can be approximated with arbitrarily high accuracy by a rational number. Therefore, we will assume that the energy changes $(\Delta E^{R'})^{\rm swrev}_{A_1A_2}$ and $(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2}$ are rational numbers, so that whatever is the value of their ratio, there exist two positive integers m and n such that $(\Delta E^{R'})^{\rm swrev}_{A_1A_2}/(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2} = n/m$, *i.e.*,

$$m\,(\Delta E^{R'})^{\rm swrev}_{A_1A_2} = n\,(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2} \quad . \tag{9}$$

Therefore, as sketched in Figure 6, let us consider the sequences Π_A and Π'_A defined as follows. Π_A is the following sequence of weight processes for the composite system $AR'R''$: starting from the initial state R'_1 of R' and R''_2 of R'', system A is brought from A_1 to A_2 by a reversible standard weight process for AR', then from A_2 to A_1 by a reversible standard weight process for AR''; whatever the new states of R' and R'' are, again system A is brought from A_1 to A_2 by a reversible standard weight process for AR' and back to A_1 by a reversible standard weight process for AR'', until the cycle for A is repeated m times. Similarly, $\Pi_{A'}$ is a sequence of weight processes for the composite system $A'R'R''$ whereby starting from the end states of R' and R'' reached by sequence Π_A, system A' is brought from A'_1 to A'_2 by a reversible standard weight process for $A'R''$, then from A'_2 to A'_1 by a reversible standard weight process for $A'R'$; and so on until the cycle for A' is repeated n times.

Clearly, the composite sequence $(\Pi_A, \Pi_A{}')$ is a cycle for AA'. Moreover, it is a cycle also for R'. In fact, on account of Theorem 2, the energy change of R' in each process $\Pi_{AR'}$ is equal to $(\Delta E^{R'})^{\rm swrev}_{A_1A_2}$ regardless of its initial state and in each process $-\Pi_{A'R'}$ is equal to $-(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2}$. Therefore, the energy change of R' in the sequence (Π_A, Π'_A) is $m\ (\Delta E^{R'})^{\rm swrev}_{A_1A_2} - n\ (\Delta E^{R'})^{\rm swrev}_{A'_1A'_2}$ and equals zero on account of Eq. (9). As a result, after (Π_A, Π'_A), reservoir R' has been restored to its initial state, so that (Π_A, Π'_A) is a reversible weight process for R''.

Again on account of Theorem 2, the overall energy change of R'' in the sequence is $-m\ (\Delta E^{R''})^{\rm swrev}_{A_1A_2} + n\ (\Delta E^{R''})^{\rm swrev}_{A_1A_2}$. If this quantity were negative, Theorem 1 would be violated. If this quantity were positive, Theorem 1 would also be violated by the reverse of the process, $(-\Pi'_A, -\Pi_A)$. Therefore, the only possibility is that $-m\ (\Delta E^{R''})^{\rm swrev}_{A_1A_2} + n\ (\Delta E^{R''})^{\rm swrev}_{A_1A_2} = 0$, *i.e.*,

$$m\ (\Delta E^{R''})^{\rm swrev}_{A_1A_2} = n\ (\Delta E^{R''})^{\rm swrev}_{A'_1A'_2}\ . \tag{10}$$

Finally, taking the ratio of Eqs. (9) and (10), we obtain Eq. (8) which is our thesis.

Temperature of a thermal reservoir. (Figure 7) Let R be a given thermal reservoir and R^o a reference thermal reservoir. Select an arbitrary pair of states (A_1, A_2) of a system A and consider the energy changes $(\Delta E^R)^{\rm swrev}_{A_1A_2}$ and $(\Delta E^{R^o})^{\rm swrev}_{A_1A_2}$ in two reversible standard weight processes from A_1 to A_2, one for AR and the other for AR^o, respectively. We call *temperature* of R the positive quantity

$$T_R = T_{R^o}\ \frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{(\Delta E^{R^o})^{\rm swrev}_{A_1A_2}}\ , \tag{11}$$

where T_{R^o} is a positive constant associated arbitrarily with the reference thermal reservoir R^o. Clearly, the temperature T_R of R is defined only up to the arbitrary multiplicative constant T_{R^o}. If for R^o we select a thermal reservoir consisting of ice, liquid water, and water vapor at triple-point conditions, and we set $T_{R^o} = 273.16$ K, we obtain the Kelvin temperature scale.

Corollary 1. The ratio of the temperatures of two thermal reservoirs, R' and R'', is independent of the choice of the reference thermal reservoir and can be measured directly as

$$\frac{T_{R'}}{T_{R''}} = \frac{(\Delta E^{R'})^{\rm swrev}_{A_1A_2}}{(\Delta E^{R''})^{\rm swrev}_{A_1A_2}}\ , \tag{12}$$

where $(\Delta E^{R'})^{\rm swrev}_{A_1A_2}$ and $(\Delta E^{R''})^{\rm swrev}_{A_1A_2}$ are the energy changes of R' and R'' in two reversible standard weight processes, one for AR' and the other for AR'', which interconnect the same pair of states (A_1, A_2).

Proof. Let $(\Delta E^{R^o})^{\rm swrev}_{A_1A_2}$ be the energy change of the reference thermal reservoir R^o in any reversible standard weight process for AR^o which interconnects the same states (A_1, A_2) of A. From Eq. (11) we have

$$T_{R'} = T_{R^o}\ \frac{(\Delta E^{R'})^{\rm swrev}_{A_1A_2}}{(\Delta E^{R^o})^{\rm swrev}_{A_1A_2}}\ ,\quad T_{R''} = T_{R^o}\ \frac{(\Delta E^{R''})^{\rm swrev}_{A_1A_2}}{(\Delta E^{R^o})^{\rm swrev}_{A_1A_2}}\ , \tag{13}$$

so that the ratio $T_{R'}/T_{R''}$ is given by Eq. (12).

Corollary 2. Let (A_1, A_2) be any pair of states of system A, and let $(\Delta E^R)^{\text{swrev}}_{A_1A_2}$ be the energy change of a thermal reservoir R with temperature T_R, in any reversible standard weight process for AR from A_1 to A_2. Then, for the given system A, the ratio $(\Delta E^R)^{\text{swrev}}_{A_1A_2}/T_R$ depends only on the pair of states (A_1, A_2), *i.e.*, it is independent of the choice of reservoir R and of its initial stable equilibrium state R_1.

Proof. Let us consider two reversible standard weight processes from A_1 to A_2, one for AR' and the other for AR'', where R' is a thermal reservoir with temperature $T_{R'}$ and R'' is a thermal reservoir with temperature $T_{R''}$. Then, equation (12) yields

$$\frac{(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}}{T_{R'}} = \frac{(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}}{T_{R''}} \quad . \tag{14}$$

Definition of (thermodynamic) entropy, proof that it is a property. Let (A_1 , A_2) be any pair of states of a system A, and let R be an arbitrarily chosen thermal reservoir placed in the environment B of A. We call *entropy difference* between A_2 and A_1 the quantity

$$S^A_2 - S^A_1 = -\frac{(\Delta E^R)^{\text{swrev}}_{A_1A_2}}{T_R} \tag{15}$$

where $(\Delta E^R)^{\text{swrev}}_{A_1A_2}$ is the energy change of R in any reversible standard weight process for AR from A_1 to A_2, and T_R is the temperature of R. On account of Corollary 2, the right hand side of Eq. (15) is determined uniquely by states A_1 and A_2; therefore, entropy is a property of A.

Let A_0 be a reference state of A, to which we assign an arbitrarily chosen value of entropy S^A_0. Then, the value of the entropy of A in any other state A_1 of A is determined uniquely by the equation

$$S^A_1 = S^A_0 - \frac{(\Delta E^R)^{\text{swrev}}_{A_0A_1}}{T_R} \quad , \tag{16}$$

where $(\Delta E^R)^{\text{swrev}}_{A_0A_1}$ is the energy change of R in any reversible standard weight process for AR from A_0 to A_1, and T_R is the temperature of R. Such a process exists for every state A_1, on account of Assumption 2.

Comment. In view of the growing revival of interest in the field of nonequilibrium thermodynamics, it is worth to emphasize that a most important consequence of the above definition (and of that proposed in 1991 by Gyftopoulos and Beretta [8], here improved) is that entropy is well and rigorously defined also for nonequilibrium states.

Theorem 4. Additivity of entropy differences. Consider the pair of states $(C_1 = A_1B_1, C_2 = A_2B_2)$ of the composite system $C = AB$. Then,

$$S^{AB}_{A_2B_2} - S^{AB}_{A_1B_1} = S^A_2 - S^A_1 + S^B_2 - S^B_1 \quad . \tag{17}$$

Proof. Let us choose a thermal reservoir R, with temperature T_R, and consider the sequence (Π_{AR}, Π_{BR}) where Π_{AR} is a reversible standard weight process for AR from A_1 to A_2, while Π_{BR} is a reversible standard weight process for BR from B_1 to B_2. The sequence $(\Pi_{AR},\, \Pi_{BR})$ is a reversible standard weight process for CR from C_1 to C_2, in which the energy change of R is the sum of the energy changes in the constituent processes Π_{AR} and Π_{BR}, *i.e.*, $(\Delta E^R)^{\rm swrev}_{C_1C_2} = (\Delta E^R)^{\rm swrev}_{A_1A_2} + (\Delta E^R)^{\rm swrev}_{B_1B_2}$. Therefore:

$$\frac{(\Delta E^R)^{\rm swrev}_{C_1C_2}}{T_R} = \frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} + \frac{(\Delta E^R)^{\rm swrev}_{B_1B_2}}{T_R} \quad . \tag{18}$$

Equation (18) and the definition of entropy (15) yield Eq. (17).

Comment. As a consequence of Theorem 4, if the values of entropy are chosen so that they are additive in the reference states, entropy results as an additive property.

Theorem 5. Let $(A_1,\, A_2)$ be any pair of states of a system A and let R be a thermal reservoir with temperature T_R. Let $\Pi_{AR{\rm irr}}$ be any irreversible standard weight process for AR from A_1 to A_2 and let $(\Delta E^R)^{\rm swirr}_{A_1A_2}$ be the energy change of R in this process. Then

$$-\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} < S^A_2 - S^A_1 \quad . \tag{19}$$

Proof. Let $\Pi_{AR{\rm rev}}$ be any reversible standard weight process for AR from A_1 to A_2 and let $(\Delta E^R)^{\rm swrev}_{A_1A_2}$ be the energy change of R in this process. On account of Theorem 2,

$$(\Delta E^R)^{\rm swrev}_{A_1A_2} < (\Delta E^R)^{\rm swirr}_{A_1A_2} \quad . \tag{20}$$

Since T_R is positive, from Eqs. (20) and (15) one obtains

$$-\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} < -\frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} = S^A_2 - S^A_1 \quad . \tag{21}$$

Theorem 6. Principle of entropy nondecrease. Let (A_1, A_2) be a pair of states of a system A and let $(A_1 \to A_2)_W$ be any weight process for A from A_1 to A_2. Then, the entropy difference $S^A_2 - S^A_1$ 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.

Proof. If $(A_1 \to A_2)_W$ is reversible, then it is a special case of a reversible standard weight process for AR in which the initial stable equilibrium state of R does not change. Therefore, $(\Delta E^R)^{\rm swrev}_{A_1A_2} = 0$ and by applying the definition of entropy, Eq. (15), one obtains

$$S^A_2 - S^A_1 = -\frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} = 0 \quad . \tag{22}$$

If $(A_1 \to A_2)_W$ is irreversible, then it is a special case of an irreversible standard weight process for AR in which the initial stable equilibrium state of R does not change. Therefore, $(\Delta E^R)^{\rm swirr}_{A_1A_2} = 0$ and Equation (19) yields

$$S^A_2 - S^A_1 > -\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} = 0 \quad . \tag{23}$$

Moreover: if a weight process $(A_1 \to A_2)_W$ for A is such that $S^A_2 - S^A_1 = 0$, then the process must be reversible, because we just proved that for any irreversible weight process $S^A_2 - S^A_1 > 0$; if a weight process $(A_1 \to A_2)_W$ for A is such that $S^A_2 - S^A_1 > 0$, then the process must be irreversible, because we just proved that for any reversible weight process $S_2^A - S_1^A = 0$.

CONCLUSIONS

A general definition of thermodynamic entropy has been presented, based on operative definitions of all the concepts employed in the treatment, designed to provide a clarifying and useful, complete and coherent, minimal but general, rigorous logical framework suitable for unambiguous fundamental discussions on Second Law implications.

Operative definitions of system, state, isolated system, separable system, environment of a system, process and system uncorrelated from its environment have been stated, which are valid also in the presence of internal semipermeable walls, reaction mechanisms and external force fields. The concepts of heat and of quasistatic process are never mentioned, so that the treatment holds also for nonequilibrium states, both for macroscopic and few particles systems.

A definition of thermal reservoir less restrictive than in previous treatments has been adopted: it is fulfilled by any single-constituent simple system contained in a fixed region of space, provided that the energy values are restricted to a suitable finite range. The proof that entropy is a property of the system has been completed by a new explicit proof that the entropy difference between two states of a system is independent of the initial state of the thermal reservoir chosen to measure it.

The definition of a reversible process has been given with reference to a given *scenario*, *i.e.*, the largest isolated system whose subsystems are available for interaction; thus, the operativity of the definition is improved and the treatment becomes compatible also with old [14] and recent [12] interpretations of irreversibility in the quantum theoretical framework. Finally, we emphasize that the fast growing field of nonequilibrium thermodynamics [16] would rest on shaky grounds without an operative definition of entropy valid also for nonequilibrium states. As well testified by this journal, research advances in nonequilibrium thermodynamics span from theory to applications in a variety of diverse fields, and seem to substantiate from many perspectives the validity of a general principle of maximum entropy production [17] wherein a clear understanding of the definition of entropy for nonequilibrium states appears to be an obvious prerequisite.

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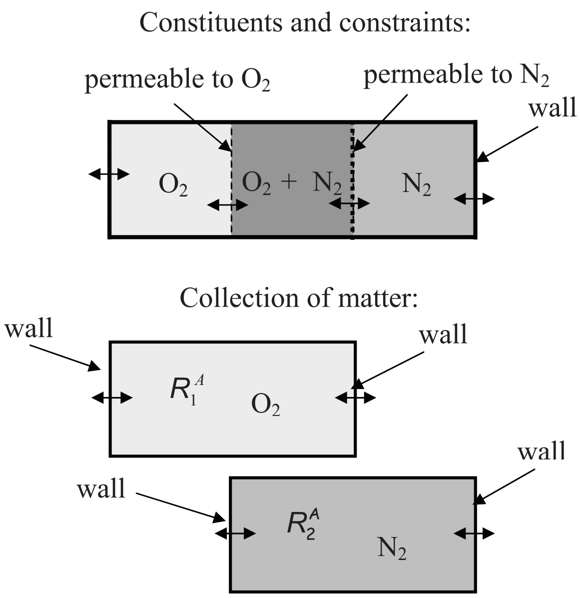


Figure 1: Collection of matter with two nonreactive constituents and two internal semipermeable membranes: the overlapping regions of space R_1^A and R_2^A are split, for clarity.

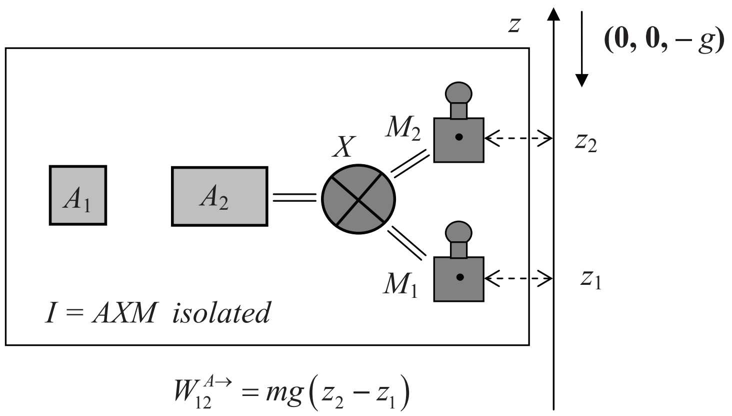


Figure 2: Schematic illustration of a weight process for system A.

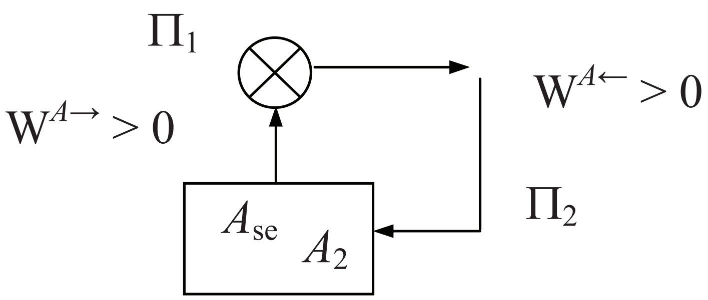


Figure 3: Schematic illustration of the proof of Theorem 1.

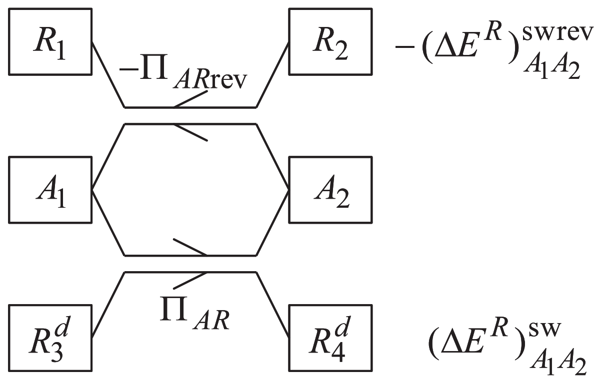
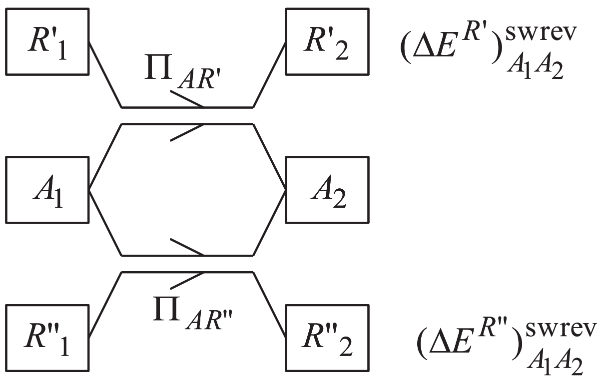


Figure 4: Illustration of the proof of Theorem 2: standard weight processes $\Pi_{AR\text{rev}}$ (reversible) and Π_{AR}; R^d is a duplicate of R; see text.



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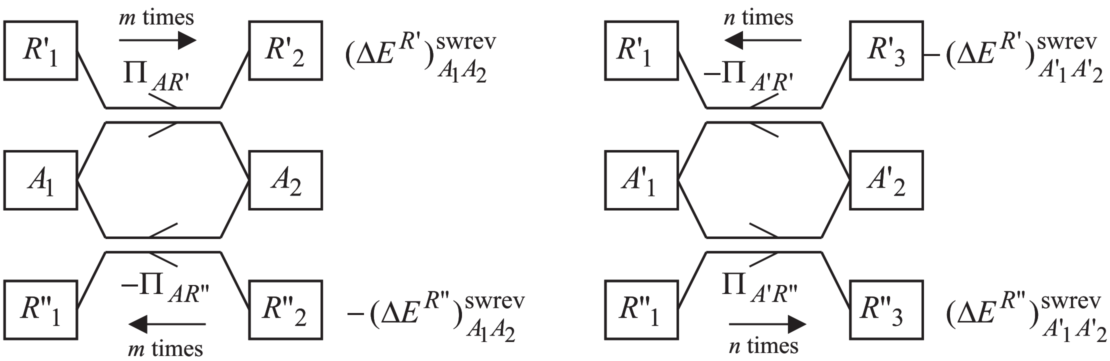

Figure 6: Illustration of the proof of Theorem 3, part b): sequence of processes (Π_A, $\Pi_{A'}$), see text.

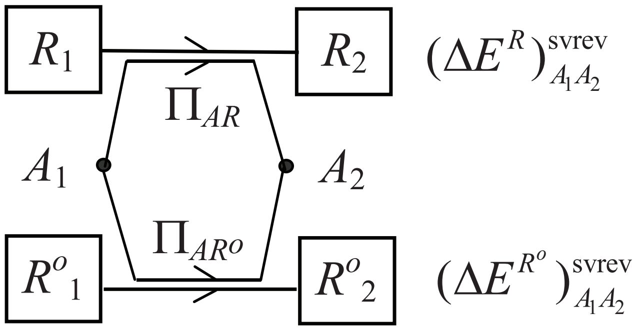

Figure 7: Schematic illustration of the processes used to define the temperature of a thermal reservoir.