RIGOROUS OPERATIONAL DEFINITION OF ENTROPY NOT BASED ON THE CONCEPTS OF HEAT AND OF EMPIRICAL TEMPERATURE

Enzo Zanchini*, Gian Paolo Beretta**

*University of Bologna – Department of Industrial Engineering
Viale Risorgimento 2, 40136 Bologna, Italy, E-mail: enzo.zanchini@unibo.it
**University of Brescia – Department of Mechanical and Industrial Engineering
Via Branze 38, 25123 Brescia, Italy, E-mail: beretta@ing.unibs.it

ABSTRACT

A rigorous and general logical scheme for the definition of entropy is presented, which is based on a complete set of operational basic definitions and is free of the unnecessary assumptions that restrict the definition of entropy to the stable equilibrium states of simple systems. The treatment applies also to systems with movable internal walls and/or semipermeable walls, and with chemical reactions and and/or external force fields. Preliminary and auxiliary to the definition of entropy are the definition of thermal reservoir and an important theorem which supports the operational definition of temperature of a thermal reservoir. Whereas the thermal reservoir must be a normal system, the definition of entropy applies, in principle, even to special systems, *i.e.*, system with both a lower and an upper bound in energy.

INTRODUCTION

From the origins of classical thermodynamics to the present time, several methods for the definitions of thermodynamic temperature and of entropy have been developed. If we exclude the treatments based on statistical mechanics and those which directly postulate the existence and additivity of entropy, as well as the structure of the fundamental relations [1], most of the methods can be divided in three main categories, which we will call as follows: classical methods, Carathéodory-derived methods, Keenan-school methods.

Classical methods start with the Zeroth-Law of thermodynamics (transitivity of mutual thermal equilibrium) and the definition of empirical temperature, then define energy by a suitable statement of the First Law, and finally define thermodynamic temperature and entropy through the Kelvin-Planck statement of the Second Law [2]: 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 thermal reservoir.

In their original formulation, classical methods had a logical loop in the definition of energy. In fact, the First Law was stated as follows: in a cycle, the work done by a system is equal to the heat received by the system,

$$Q = W \ . \tag{1}$$

The energy difference between state A_2 and state A_1 of a system A was defined as the value of $Q-W$ for A in any process of A from A_1 to A_2. Clearly, this definition is vitiated by a logical circularity, because it is impossible to define heat without a previous definition of energy.

The circularity of Eq. (1) 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.

Among the best treatments of thermodynamics by the classical method we can quote, for instance, those by Fermi [4] and by Zemansky [5].

In his celebrated paper [3], Carathéodory proposed also a new statement of the Second Law and developed a completely new method for the definitions of thermodynamic temperature and entropy. The treatment refers to simple systems, stable equilibrium states, and quasistatic processes, *i.e.*, processes in which the system evolves along a sequence of stable equilibrium states. A simple system is defined as a system such that:
a) its stable equilibrium states are determined uniquely by $n+1$ coordinates, $\xi_0, x_1, ..., x_n$, where $x_1, ..., x_n$ are deformation coordinates (*i.e.*, coordinates which determine the external shape of the system), while ξ_0 is not a deformation coordinate.
b) in every quasistatic reversible process, the work performed by the system is given by

$$\delta W = p_1\,\mathrm{d}x_1 + ... + p_n\,\mathrm{dx_n} \ , \tag{2}$$

where p_1, ... , p_n are functions of $\xi_0, x_1, ..., x_n$;
c) the (internal) energy U of the system is additive, *i.e.*, equals the sum of the energies of its subsystems.

Carathéodory stated the Second Law (Axiom II) as follows: in every arbitrarily close neighborhood of a given initial state there exist states that cannot be reached by adiabatic processes. Then, by employing a mathematical theorem on Pfaffian equations, he proved that, on account of the Second Law, there exists a pair of properties, $M(\xi_0, x_1, ..., x_n)$ and $x_0(\xi_0, x_1, ..., x_n)$, such that for every quasistatic process

$$\mathrm{d}U + \delta W = M\,\mathrm{d}x_0 \ . \tag{3}$$

Through other assumptions on the conditions for mutual stable equilibrium, which include the Zeroth Law (transitivity of mutual stable equilibrium), Carathéodory proved that there exists a function $\tau(x_0, x_1, ..., x_n)$, called temperature, such that if two systems A and B are in mutual stable equilibrium they have the same temperature. Moreover, by applying the additivity of energy, he proved that there exists a function $f(\tau)$, identical for all systems, such that

$$M = f(\tau)\,\alpha(x_0) \ , \tag{4}$$

where $\alpha(\cdot)$ is another function that varies from system to system.

Finally, he defined thermodynamic temperature T and entropy S as

$$T = c f(\tau) \ , \ S - S_{\text{ref}} = \int_{x_0|_{\text{ref}}}^{x_0} \frac{\alpha(x_0')}{c}\, \mathrm{d}x_0' \ , \tag{5}$$

where c is an arbitrary constant and S_{ref} an arbitrary value assigned to the reference state with $x_0 = x_0|_{\text{ref}}$, and rewrote Eq. (3) in the form

$$\mathrm{d}U + \delta W = T\,\mathrm{d}S \ . \tag{6}$$

Although mathematically very elegant, Carathéodory's definition of entropy is rather abstract. For this reason, several authors proposed simplifications of Carathéodory's treatment [6; 7; 8].

On the opposite side, more recently, Lieb and Yngvason [9] developed a new treatment of the foundations of thermodynamics which can be classified among the Carathéodory-derived ones, because the key postulates concern adiabatic accessibility, but is more abstract and complex than the original presentation by Carathéodory. The treatment is based on 15 Axioms, which regard adiabatic accessibility, simple systems, thermal equilibrium, mixtures and reactions. The treatment by Lieb and Yngvason, like that by Carathéodory, refers exclusively to stable equilibrium states of simple systems.

An alternative method for the treatment of the foundations of thermodynamics was introduced by Keenan [10] and developed by Hatsopoulos and Keenan [11], by Gyftopoulos and Beretta [12], and, more recently, by Beretta and Zanchini [13; 14]. The treatments developed along this line of thought will be called Keenan-school methods.

Some advantages of the Keenan-school methods, with respect to the Carathéodory-derived ones, are the following:
a) careful *operational* definitions of all the concepts employed in the theory are given; thus, the definition of entropy is completely free of ambiguities, and an operational procedure to measure entropy differences is clearly stated;
b) the treatment does not employ the concepts of simple system and of quasistatic process, so that it is not necessarily restricted to the stable equilibrium states of simple systems.

A disadvantage is the use, in analogy with the classical methods, of the concept of thermal reservoir, which, however, is defined rigorously. This disadvantage will be removed in a research work under development.

In this paper, some improvements of the method developed in Refs. [13; 14] are introduced. In particular, the statements of the First Law and of the Second Law are split in parts, to form 5 independent Assumptions. This is done because the domain of validity could be different for different Assumptions. Moreover, the restriction to normal systems is released. The treatment presented here refers exclusively to closed systems. A rigorous extension of the definitions of energy and entropy to open systems can be found, for instance, in Ref. [14].

SUMMARY OF BASIC DEFINITIONS

We briefly recall here some definitions of the basic concepts of thermodynamics employed in our treatment. A more complete and more detailed set of operational basic definitions can be found in Refs. [13; 14].

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. If the boundary surfaces of the regions of space which contain the particles of the systems are all *walls*, *i.e.*, surfaces which cannot be crossed by material particles, the system is called *closed*.

Any system is endowed with a set of reproducible measurement procedures such that each procedure, if applied at an instant t, yields a result which is independent of the previous time evolution of the system; each procedure of this kind defines a *property* of the system. 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.

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.

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 touch 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.

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 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.

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 only for the states of A such that A is separable and uncorrelated from its environment.

We call *process* of a system A from state A_1 to state A_2 the time evolution $(AB)_1 \rightarrow (AB)_2$ 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. A process of A is *reversible* if the isolated system AB can undergo a time evolution $(AB)_2 \to (AB)_1$, which restores it in its initial state $(AB)_1$ and is called *reverse* of $(AB)_1 \to (AB)_2$. 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.

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.

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 bound the regions of space $\boldsymbol{R}^A$ 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.

DEFINITION OF ENERGY FOR A CLOSED SYSTEM

Assumption 1. First Law Statement - Part 1. The works done by a system in any two weight processes between the same initial and final states are identical.

Assumption 2. First Law Statement - Part 2. 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 process for A.

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 closed system A, such that A is separable from its environment in both states. 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 $W_{21}^{A\rightarrow}$ done by A in any weight process from A_2 to A_1; in symbols:

$$E_2^A - E_1^A = W_{12}^{A\leftarrow} \quad \text{or} \quad E_2^A - E_1^A = W_{21}^{A\rightarrow} . \tag{7}$$

The First Law yields the following consequences:
(*a*) if both weight processes $A_1 \xrightarrow{\text{w}} A_2$ and $A_2 \xrightarrow{\text{w}} A_1$ exist, the two forms of Eq. (7) 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 $(AB)_1$ and $(AB)_2$ of a composite system AB, where both A and B are closed, 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,

$$E_2^{AB} - E_1^{AB} = E_2^A - E_1^A + E_2^B - E_1^B \ ; \tag{8}$$

(*d*) (*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 either

$$E_1^A = E_0^A + W_{01}^{A\leftarrow} \quad \text{or} \quad E_1^A = E_0^A + W_{10}^{A\rightarrow} \ , \tag{9}$$

where $W_{01}^{A\leftarrow}$ is the work received by A in any weight process for A from A_0 to A_1, and $W_{10}^{A\rightarrow}$ is the work performed by A in any weight process for A from A_1 to A_0.

Rigorous proofs of these consequences can be found in Refs. [12; 15], and will not be repeated here.

DEFINITION OF ENTROPY FOR A CLOSED SYSTEM

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 $\boldsymbol{R}^A$ and the same value of the energy E^A.

Proof. Since A is closed and in any stable equilibrium state it is separable 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 change of the regions of space $\boldsymbol{R}^A$ and no change of the state of the environment of A, and hence would not satisfy the definition of stable equilibrium state.

Normal System. Every closed system A whose energy is bounded from below and unbounded from above will be called a *normal system*.

Assumption 3. Second Law Statement - Part 1. Starting from any state, a normal system can be changed to a non-equilibrium state with higher energy by means of a weight process for A in which its regions of space have no net changes.

Comment. The additivity of energy implies that the union of two or more normal systems, each separable from its environment, is a normal system, and thus fulfils Assumption 3.

In traditional treatments of thermodynamics, Assumption 3 is *not stated explicitly*, but 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 Fig 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 $\boldsymbol{R}^A$ occupied by the constituents of A have no net change. On account of Assumption 3, 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

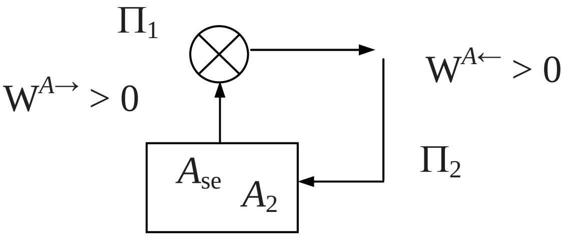

Figure 1. Illustration of the proof of Theorem 1.

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.

Assumption 4. Second Law Statement - Part 2. Among all the states of a closed 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 2. Any stable equilibrium state A_{se} of a closed system A is accessible via an irreversible zero-work weight process from any other state A_1 in which A is separable from its environment, occupies the same regions of space $\boldsymbol{R}^A$ and has the same value of the energy E^A.

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

Corollary 1. Any state in which a closed system A is separable from its environment can be changed to a unique stable equilibrium state by means of a zero-work weight process for A in which the regions of space $\boldsymbol{R}^A$ have no net change.

Proof. The thesis follows immediately from Assumption 4, Lemma 1 and Lemma 2.

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 normal 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 normal 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. [12, 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 an excellent approximation of a thermal reservoir.

Indeed, for a system of this kind, when three different phases (such as, solid, liquid and vapor) are present, two stable equilibrium states with different energy values have, with an extremely high approximation, the same temperature (here not yet defined), and thus fulfil the condition for the mutual stable equilibrium of the system and a copy thereof.

Reference thermal reservoir. A thermal reservoir chosen once and for all is called a *reference thermal reservoir*. To fix ideas, we 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 closed 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 $(A_1R_1 \rightarrow A_2R_2)^{\mathrm{sw}}$ a standard weight process for AR from A_1 to A_2 and by $(\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$ the corresponding energy change of the thermal reservoir R.

Assumption 5. Second Law Statement - Part 3. Every pair of states (A_1, A_2) of a closed system A, such that A is separable and uncorrelated from its environment in both states, can be interconnected by a reversible standard weight process for AR, where R is an arbitrarily chosen thermal reservoir.

Comment. The combination of Assumption 5, Assumption 4 and Lemma 1 forms our re-statement of the *Gyftopoulos-Beretta statement of the Second Law* [12, p. 62-63]. The motivation for the separation of the statement proposed in Ref. [12] into three parts 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*.

Theorem 2. For a given closed system A and a given thermal reservoir R, among all the standard weight processes for AR between a given pair of states (A_1, A_2) of A in which A is separable and uncorrelated from its environment, the energy change $(\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$ 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 $\Pi_{AR\mathrm{rev}}$ a reversible one; the energy changes of R in processes Π_{AR} and $\Pi_{AR\mathrm{rev}}$ are, respectively, $(\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$ and $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2}$. With the help of Fig 2, we will prove that, regardless of the initial state of R:

a) $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2} \leq (\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$;

b) if also Π_{AR} is reversible, then $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2} = (\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$;

c) if $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2} = (\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$, 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 $\Pi_{AR\mathrm{rev}}$. 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 $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2} > (\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$, and consider the composite process $(-\Pi_{AR\mathrm{rev}}, \Pi_{AR})$, where $-\Pi_{AR\mathrm{rev}}$ is a reverse of $\Pi_{AR\mathrm{rev}}$. This process would be a weight process for RR^d in which, starting from the stable equilibrium state $R_2R^d_3$,

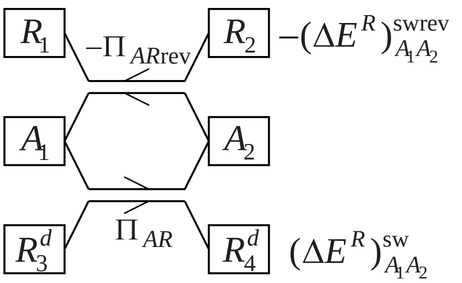

Figure 2. Illustration of the proof of Theorem 2: $-\Pi_{AR\text{rev}}$ is a reverse of the reversible standard weight processes $\Pi_{AR\text{rev}}$, and R^d is a duplicate of R; see text.

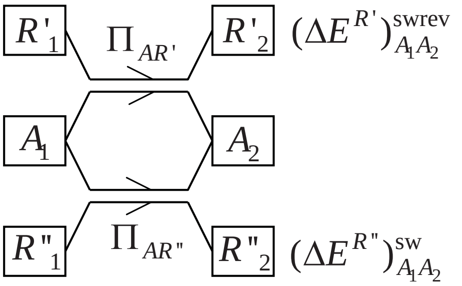

Figure 3. Illustration of the proof of Theorem 3, part a): reversible standard weight processes $\Pi_{AR'}$ and $\Pi_{AR''}$, see text.

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 composite process ($\Pi_{AR\text{rev}}$, $-\Pi_{AR}$) 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 composite process (Π_{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 closed system A, such that A is separable and uncorrelated from its environment in both states. 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 Fig 3, 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 composite process ($\Pi_{AR'}$, $-\Pi_{AR''}$), 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

$$W^{R'R''\to} = -(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} + (\Delta E^{R''})^{\text{swrev}}_{A_1A_2} \ , \tag{10}$$

where both terms are positive. On account of Assumption 3 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 $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$ is given back to R'' and the latter is restored to its initial stable equilibrium state. As a result, the composite process ($\Pi_{AR'}$, $-\Pi_{AR''}$, $\Pi_{R''}$) 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 $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} < 0$ implies $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} < 0$.

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

Proof of b). Choose a pair of states (A_1, A_2) of a closed system A, such that A is separable and uncorrelated from its environment, and consider the reversible standard weight process $\Pi_{AR'} = (A_1R'_1 \to A_2R'_2)^{\text{swrev}}$ for AR', with R' initially in state R'_1, and the reversible standard weight process $\Pi_{AR''} = (A_1R''_1 \to A_2R''_2)^{\text{swrev}}$ for AR'', with R'' initially in state R''_1. Then, choose a pair of states (A'_1, A'_2) of another closed system A', such that A' is separable and uncorrelated from its environment, and consider the reversible standard weight process $\Pi_{A'R'} = (A'_1R'_1 \to A'_2R'_3)^{\text{swrev}}$ for $A'R'$, with R' initially in state R'_1, and the reversible standard weight process $\Pi_{A'R''} = (A'_1R''_1 \to A'_2R''_3)^{\text{swrev}}$ for $A'R''$, with R'' initially in state R''_1.

With the help of Fig 4, we will prove that the changes in energy of the reservoirs in these processes obey the relation

$$\frac{(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}}{(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}} = \frac{(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2}}{(\Delta E^{R''})^{\text{swrev}}_{A'_1A'_2}} \ . \tag{11}$$

Let us assume: $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} > 0$ and $(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2} > 0$, which implies, on account of part a) of the proof, $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} > 0$ and $(\Delta E^{R''})^{\text{swrev}}_{A'_1A'_2} > 0$. This is not a restriction, because it is possible to reverse the processes under consideration.

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 $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}$ and $(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2}$ are rational numbers, so that whatever is the value of their ratio, there exist two positive integers m and n such that

$(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}/(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2} = n/m$, *i.e.*,

$$m\,(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} = n\,(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2} \ . \tag{12}$$

As sketched in Fig 4, let us consider the composite processes Π_A and Π'_A defined as follows. Π_A is the following composite weight process 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 composite weight process for the composite system $A'R'R''$ whereby starting from the end states of R' and R'' reached by process 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 whole composite process $(\Pi_A, \Pi_A{}')$ 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 $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}$, regardless of its initial state, and in each process $-\Pi_{A'R'}$ is equal to $-(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2}$. Therefore, the energy change of R' in the whole composite process (Π_A, Π'_A) is $m\,(\Delta E^{R'})^{\text{swrev}}_{A_1A_2} - n\,(\Delta E^{R'})^{\text{swrev}}_{A'_1A'_2}$ and equals zero on account of Eq. (12). 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 whole composite process is $-m\,(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} + n\,(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$. 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 $-m\,(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} + n\,(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} = 0$, *i.e.*,

$$m\,(\Delta E^{R''})^{\text{swrev}}_{A_1A_2} = n\,(\Delta E^{R''})^{\text{swrev}}_{A'_1A'_2} \ . \tag{13}$$

Finally, taking the ratio of Eqs. (12) and (13), we obtain Eq. (11) which is our conclusion.

Temperature of a thermal reservoir. 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 closed system A, such that A is separable and uncorrelated from its environment in both states, and consider the energy changes $(\Delta E^{R})^{\text{swrev}}_{A_1A_2}$ and $(\Delta E^{R^o})^{\text{swrev}}_{A_1A_2}$ 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

$$T_R = T_{R^o}\,\frac{(\Delta E^{R})^{\text{swrev}}_{A_1A_2}}{(\Delta E^{R^o})^{\text{swrev}}_{A_1A_2}} \ , \tag{14}$$

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 2. 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

$$\frac{T_{R'}}{T_{R''}} = \frac{(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}}{(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}} \ , \tag{15}$$

where $(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}$ and $(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}$ 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) such that A is separable and uncorrelated from its environment in both states.

Proof. Let $(\Delta E^{R^o})^{\text{swrev}}_{A_1A_2}$ 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. (14) we have

$$T_{R'} = T_{R^o}\,\frac{(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}}{(\Delta E^{R^o})^{\text{swrev}}_{A_1A_2}} \ , \quad T_{R''} = T_{R^o}\,\frac{(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}}{(\Delta E^{R^o})^{\text{swrev}}_{A_1A_2}} \ , \tag{16}$$

so that the ratio $T_{R'}/T_{R''}$ is given by Eq. (15).

Corollary 3. Let (A_1, A_2) be any pair of states of a closed system A, such that A is separable and uncorrelated from its environment in both states, 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 (15) yields

$$\frac{(\Delta E^{R'})^{\text{swrev}}_{A_1A_2}}{T_{R'}} = \frac{(\Delta E^{R''})^{\text{swrev}}_{A_1A_2}}{T_{R''}} \ . \tag{17}$$

Definition of (thermodynamic) entropy, proof that it is a property. Let $(A_1\,, A_2)$ be any pair of states of a closed system A, such that A is separable and uncorrelated from its environment in both states, 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

$$S^A_2 - S^A_1 = -\frac{(\Delta E^{R})^{\text{swrev}}_{A_1A_2}}{T_R} \ , \tag{18}$$

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

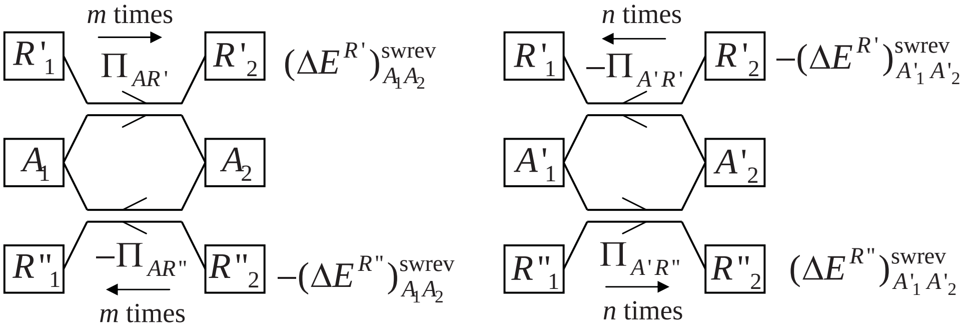

Figure 4. Illustration of the proof of Theorem 3, part b): composite process (Π_A, $\Pi_{A'}$), see text.

temperature of R. On account of Corollary 3, the right hand side of Eq. (18) 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, in which A is separable and uncorrelated from its environment, and assign to A_0 an arbitrarily chosen value S_0^A of the entropy. Then, the value of the entropy of A in any other state A_1 of A in which A is separable and uncorrelated from its environment is determined uniquely by the equation

$$S_1^A = S_0^A - \frac{(\Delta E^R)^{\rm swrev}_{A_0A_1}}{T_R} \;, \tag{19}$$

where $(\Delta E^R)^{\rm swrev}_{A_0A_1}$ 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 5.

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 $C = AB$, such that A and B are closed, A is separable and uncorrelated from its environment in both states A_1 and A_2, and B is separable and uncorrelated from its environment in both states B_1 and B_2. Then,

$$S^{AB}_{A_2B_2} - S^{AB}_{A_1B_1} = S_2^A - S_1^A + S_2^B - S_1^B \;. \tag{20}$$

Proof. Let us choose a thermal reservoir R, with temperature T_R, and consider the composite process (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 composite process (Π_{AR}, Π_{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:

$$\frac{(\Delta E^R)^{\rm swrev}_{C_1C_2}}{T_R} = \frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} + \frac{(\Delta E^R)^{\rm swrev}_{B_1B_2}}{T_R} \;. \tag{21}$$

Equation (21) and the definition of entropy (18) yield Eq. (20).

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 closed system A, such that A is separable and uncorrelated from its environment in both states, 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

$$-\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} < S_2^A - S_1^A \;. \tag{22}$$

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,

$$(\Delta E^R)^{\rm swrev}_{A_1A_2} < (\Delta E^R)^{\rm swirr}_{A_1A_2} \;. \tag{23}$$

Since T_R is positive, from Eqs. (23) and (18) one obtains

$$-\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} < -\frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} = S_2^A - S_1^A \;. \tag{24}$$

Theorem 6. Principle of entropy nondecrease. Let (A_1, A_2) be a pair of states of a closed system A, such that A is separable and uncorrelated from its environment in both states, and let $(A_1 \to A_2)_W$ be any weight process for A from A_1 to A_2. Then, the entropy difference $S_2^A - S_1^A$ 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.

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. (18), one obtains

$$S_2^A - S_1^A = -\frac{(\Delta E^R)^{\rm swrev}_{A_1A_2}}{T_R} = 0 \;. \tag{25}$$

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 (22) yields

$$S_2^A - S_1^A > -\frac{(\Delta E^R)^{\rm swirr}_{A_1A_2}}{T_R} = 0 \;. \tag{26}$$

Moreover, if a weight process $(A_1 \to A_2)_W$ 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 $(A_1 \to A_2)_W$ 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 $S_2^A - S_1^A = 0$.

CONCLUSIONS

A rigorous and general logical scheme for the definition of entropy has been presented. The treatment is based on a complete set of operational definitions and does not employ the concepts of empirical temperature, of heat, of simple system and of quasistatic process. Therefore, in this scheme, the domain of validity of the definition of entropy is not constrained necessarily to the stable equilibrium states of simple systems. On the other hand, the important concepts of separability and non-correlation between system and environment have been introduced and the role of these concepts in the definitions of energy and of entropy has been pointed out.

With respect to previous presentations of this approach, some improvements have been introduced. The statements of the First Law and of the Second Law have been split in 5 separate Assumptions, each of which may have his own domain of validity. Moreover, the restriction to normal systems in the definition of entropy has been removed, so that the definition applies, in principle, also to special systems, such as spin systems.

REFERENCES

[1] H.B. Callen, *Thermodynamics*, Wiley, New York, N.Y., 1960.

[2] M. Planck, *Treatise on Thermodynamics*, translated by A. Oggs from the 7th German edition, Longmans, Green, and Co., London, U.K., 1927 (the first german edition appeared in 1897).

[3] C. Carathéodory, Untersuchungen über die Grundlagen der Thermodynamik, *Math. Ann.*, vol. 67, pp. 355-389, 1909.

[4] E. Fermi, *Thermodynamics*, Prentice-Hall, New Jersey, 1937.

[5] M.W. Zemansky, *Heat and Thermodynamics*, Mc Graw-Hill, New York, N.Y., 1968.

[6] L.A. Turner, Simplification of Carathéodory's treatment of thermodynamics, *Am. J. Phys.*, vol. 28, pp. 781-786, 1960.

[7] P.T. Landsberg, On suggested simplifications of Carathéodory's thermodynamics, *Phys. Status Solidi* (*b*), vol. 1, pp. 120-126, 1961.

[8] F.W. Saers, A simplified simplification of Carathéodory's thermodynamics, *Am. J. Phys.*, vol. 31, pp. 747-752, 1963.

[9] E.H. Lieb and J. Yngvason, The physics and mathematics of the second law of thermodynamics, *Phys. Rep.*, vol. 310, pp. 1-96, 1999.

[10] J.H. Keenan, *Thermodynamics*, Wiley, New York, N.Y., 1941.

[11] G.N. Hatsopoulos and J.H. Keenan, *Principles of General Thermodynamics*, Wiley, New York, N.Y., 1965.

[12] E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics. Foundations and Applications*, Dover, Mineola, N.Y., 2005 (first edition, Macmillan, 1991).

[13] E. Zanchini and G.P. Beretta, Removing Heat and Conceptual Loops from the Definition of Entropy, *Int. J. Thermodynamics*, vol. 12, pp. 67-76, 2010.

[14] G.P. Beretta and E. Zanchini, Rigorous and General Definition of Thermodynamic Entropy, in *Thermodynamics*, Edited by Mizutani Tadashi, Publisher: InTech, 2011, ISBN 978-953-307-544-0, 23-50 (2011), eprint: ArXiv-1010.0813v1.

[15] E. Zanchini, On the Definition of Extensive Property Energy by the First Postulate of Thermodynamics, *Found. Phys.*, vol. 16, pp. 923-935, 1986.