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Rigorous and General Definition of Thermodynamic Entropy

Gian Paolo Beretta
Università di Brescia, Via Branze 38, Brescia, Italy

Enzo Zanchini
Università di Bologna, Viale Risorgimento 2, Bologna, Italy

The physical foundations of a variety of emerging technologies — ranging from the applications of quantum entanglement in quantum information to the applications of nonequilibrium bulk and interface phenomena in microfluidics, biology, materials science, energy engineering, etc. — require understanding thermodynamic entropy beyond the equilibrium realm of its traditional definition. This paper presents a rigorous logical scheme that provides a generalized definition of entropy free of the usual unnecessary assumptions which constrain the theory to the equilibrium domain. The scheme is based on carefully worded operative definitions for all the fundamental concepts employed, including those of system, property, state, isolated system, environment, process, separable system, system uncorrelated from its environment, and parameters of a system. The treatment considers also systems with movable internal walls and/or semipermeable walls, with chemical reactions and/or external force fields, and with small numbers of particles. The definition of reversible process is revised by introducing the new concept of scenario. The definition of entropy involves neither the concept of heat nor that of quasistatic process; it applies to both equilibrium and nonequilibrium states. The role of correlations on the domain of definition and on the additivity of energy and entropy is discussed: it is proved that energy is defined and additive for all separable systems, while entropy is defined and additive only for separable systems uncorrelated from their environment; decorrelation entropy is defined. The definitions of energy and entropy are extended rigorously to open systems. Finally, to complete the discussion, the existence of the fundamental relation for stable equilibrium states is proved, in our context, for both closed and open systems.

I. INTRODUCTION

Thermodynamics and Quantum Theory are among the few sciences involving fundamental concepts and universal content that are controversial and have been so since their birth, and yet continue to unveil new possible applications and to inspire new theoretical unification. The basic issues in Thermodynamics have been, and to a certain extent still are: the range of validity and the very formulation of the Second Law of Thermodynamics, the meaning and the definition of entropy, the origin of irreversibility, and the unification with Quantum Theory [19]. The basic issues with Quantum Theory have been, and to a certain extent still are: the meaning of complementarity and in particular the wave-particle duality, understanding the many faces of the many wonderful experimental and theoretical results on entanglement, and the unification with Thermodynamics [22].

Entropy has a central role in this situation. It is astonishing that after over 140 years since the term entropy has been first coined by Clausius [11], there is still so much discussion and controversy about it, not to say confusion. Two recent conferences, both held in October 2007, provide a state-of-the-art scenario revealing an unsettled and hard to settle field: one, entitled *Meeting the entropy challenge* [6], focused on the many physical aspects (statistical mechanics, quantum theory, cosmology, biology, energy engineering), the other, entitled *Facets of entropy* [18], on the many different mathematical concepts that in different fields (information theory, communication theory, statistics, economy, social sciences, optimization theory, statistical mechanics) have all been termed *entropy* on the basis of some analogy of behavior with the *thermodynamic entropy.*

Following the well-known Statistical Mechanics and Information Theory interpretations of thermodynamic entropy, the term *entropy* is used in many different contexts wherever the relevant *state description* is in terms of a probability distribution over some set of possible events which characterize the *system description.* Depending on the context, such events may be *microstates*, or *eigenstates*, or *configurations*, or *trajectories*, or *transitions*, or *mutations*, and so on. Given such a probabilistic description, the term entropy is used for some functional of the probabilities chosen as a quantifier of their *spread* according to some reasonable set of defining axioms [26]. In this sense, the use of a common name for all the possible different state functionals that share such broad defining features, may have some unifying advantage from a broad conceptual point of view, for example it may suggest analogies and inter-breeding developments between very different fields of research sharing similar probabilistic descriptions.

However, from the physics point of view, entropy — the *thermodynamic entropy* — is a single definite property of every well-defined material system that can be measured in every laboratory by means of standard measurement procedures. Entropy is a property of paramount practical importance, because it turns out [17] to be monotonically related to the difference $E - \Psi$ between the energy E of the system, above the lowest-energy state, and the adiabatic availability Ψ of the system, *i.e.*, the maximum work the system can do in a process which produces no other external effects. It is therefore very important that whenever we talk or make inferences about physical (*i.e.*, thermodynamic) entropy, we first agree on a precise definition.

In our opinion, one of the most rigorous and general axiomatic definitions of thermodynamic entropy available in the literature is that given in [17], which extends to the nonequilibrium domain one of the best traditional treatments available in the literature, namely that presented by Fermi [12].

In this paper, the treatment presented in [17] is assumed as a starting point and the following improvements are introduced. The basic definitions of system, state, isolated system, environment, process, separable system, and parameters of a system are deepened, by developing a logical scheme outlined in [37, 38]. Operative and general definitions of these concepts are presented, which are valid also in the presence of internal semipermeable walls and reaction mechanisms. The treatment of [17] is 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 view of the important role of entanglement in the ongoing and growing interplay between Quantum Theory and Thermodynamics, the effects of correlations on the additivity of energy and entropy are discussed and clarified. Moreover, the definition of a reversible process is given with reference to a given *scenario*; the latter is the largest isolated system whose subsystems are available for interaction, for the class of processes under exam.

Without introducing the quantum formalism, the approach is nevertheless compatible with it (and indeed, it was meant to be so, see, *e.g.*, Beretta [2, 3, 4, 5], Beretta et al. [8, 9], Hatsopoulos & Gyftopoulos [20]); it is therefore suitable to provide a basic logical framework for the recent scientific revival of thermodynamics in Quantum Theory [quantum heat engines [31, 32], quantum Maxwell demons [14, 27, 28], quantum erasers [24, 33], etc.] as well as for the recent quest for quantum mechanical explanations of irreversibility [see, *e.g.*, Bennett [1], Hatsopoulos & Beretta [19], Lloyd [29], Maccone [30]].

The paper is organized as follows. In Section II we discuss the drawbacks of the traditional definitions of entropy. In Section III we introduce and discuss a full set of basic definitions, such as those of system, state, process, etc. that form the necessary unambiguous background on which to build our treatment. In Section IV we introduce the statement of the First Law and the definition of energy. In Section V we introduce and discuss the statement of the Second Law and, through the proof of three important theorems, we build up the definition of entropy. In Section VI we briefly complete the discussion by proving in our context the existence of the fundamental relation for the stable equilibrium states and by defining temperature, pressure, and other generalized forces. In Section VII we extend our definitions of energy and entropy to the model of an open system. In Section VIII we prove the existence of the fundamental relation for the stable equilibrium states of an open system. In Section IX we draw our conclusions and, in particular, we note that nowhere in our construction we use or need to define the concept of *heat*.

II. DRAWBACKS OF THE TRADITIONAL DEFINITIONS OF ENTROPY

In traditional expositions of thermodynamics, entropy is defined in terms of the concept of heat, which in turn is introduced at the outset of the logical development in terms of heuristic illustrations based on mechanics. For example, in his lectures on physics, Feynman [13] describes heat as one of several different forms of energy related to the jiggling motion of particles stuck together and tagging along with each other (pp. 1-3 and 4-2), a form of energy which really is just kinetic energy — internal motion (p. 4-6), and is measured by the random motions of the atoms (p. 10-8). Tisza [34] argues that such slogans as "heat is motion", in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value.

There are at least three problems with these illustrations. First, work and heat are not stored in a system. Each is a mode of transfer of energy from one system to another. Second, concepts of mechanics are used to justify and make plausible a notion — that of heat — which is beyond the realm of mechanics; although at a first exposure one might find the idea of *heat as motion* harmless, and even natural, the situation changes drastically when the notion of heat is used to define entropy, and the logical loop is completed when entropy is shown to imply a host of results about energy availability that contrast with mechanics. Third, and perhaps more important, heat is a mode of energy (and entropy) transfer between systems that are very close to thermodynamic equilibrium and, therefore, any definition of entropy based on heat is bound to be valid only at thermodynamic equilibrium.

The first problem is addressed in some expositions. Landau and Lifshitz [25] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim [16] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [23] defines heat as the energy transferred from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. Similar definitions are adopted in most other notable textbooks that are too many to list.

None of these definitions, however, addresses the basic problem. The existence of exchanges of energy that differ from work is not granted by mechanics. Rather, it is one of the striking results of thermodynamics, namely, of the existence of entropy as a property of matter. As pointed out by Hatsopoulos and Keenan [21], without the

Second Law heat and work would be indistinguishable; moreover, the most general kind of interaction between two systems which are very far from equilibrium is neither a heat nor a work interaction. Following Guggenheim it would be possible to state a rigorous definition of heat, with reference to a very special kind of interaction between two systems, and to employ the concept of heat in the definition of entropy [16]. However, Gyftopoulos and Beretta [17] have shown that the concept of heat is unnecessarily restrictive for the definition of entropy, as it would confine it to the equilibrium domain. Therefore, in agreement with their approach, we will present and discuss a definition of entropy where the concept of heat is not employed.

Other problems are present in most treatments of the definition of entropy available in the literature:

1. many basic concepts, such as those of system, state, property, isolated system, environment of a system, adiabatic process are not defined rigorously;
2. on account of unnecessary assumptions (such as, the use of the concept of quasistatic process), the definition holds only for stable equilibrium states [10], or for systems which are in local thermodynamic equilibrium [12];
3. in the traditional logical scheme [10, 12, 16, 21, 23, 25, 34], some proofs are incomplete.

To illustrate the third point, which is not well known, let us refer to the definition in [12], which we consider one of the best traditional treatments available in the literature. In order to define the thermodynamic temperature, 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. In our treatment, instead, a similar statement is made explicit, and proved.

III. BASIC DEFINITIONS

Level of description, constituents, amounts of constituents, deeper level of description. We will call *level of description* a class of physical models whereby all that can be said about the matter contained in a given region of space R, at a time instant t, can be described by assuming that the matter consists of a set of elementary building blocks, that we call *constituents*, immersed in the electromagnetic field. 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*.

For instance, at the *chemical level of description* the constituents are the different chemical species, i.e., atoms, molecules, and ions; at the *atomic level of description* the constituents are the atomic nuclei and the electrons; at the *nuclear level of description* they are the protons, the neutrons, and the electrons.

The particle-like nature of the constituents implies that a counting measurement procedure is always defined and, when performed in a region of space delimited by impermeable walls, it is *quantized* in the sense that the measurement outcome is always an integer number, that we call the *number of particles*. If the counting is selective for the i-th type of constituent only, we call the resulting number of particles the *amount of constituent i* and denote it by n_i. When a number-of-particle counting measurement procedure is performed in a region of space delimited by at least one ideal-surface patch, some particles may be found across the surface. Therefore, an outcome of the procedure must also be the sum, for all the particles in this boundary situation, of a suitably defined fraction of their spatial extension which is within the given region of space. As a result, the *number of particles* and the *amount of constituent i* will not be quantized but will have continuous spectra.

A level of description L_2 is called *deeper* than a level of description L_1 if the amount of every constituent in L_2 is conserved for all the physical phenomena considered, whereas the same is not true for the constituents in L_1. For instance, the atomic level of description is deeper than the chemical one (because chemical reaction mechanisms do not conserve the number of molecules of each type, whereas they conserve the number of nuclei of each type as well as the number of electrons).

Levels of description typically have a hierarchical structure whereby the constituents of a given level are aggregates of the constituents of a deeper level.

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 of the boundary surface of R_i and its permeability topology nature (walls, ideal surfaces) can vary in time, as well as the number of particles contained in R_i.

Collection of matter, composition. We will 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, $\boldsymbol{R}^A = R_1^A, \ldots, R_i^A, \ldots, R_r^A$, each of which contains n_i^A particles of a single kind of constituent. The regions of space $\boldsymbol{R}^A$ 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. If, due to time changes, two regions of space which contain the same kind of constituent begin to overlap, from that instant a new collection of matter must be considered.

Comment. This method of description allows to consider the presence of internal walls and/or internal *semipermeable* membranes, *i.e.*, surfaces which can be crossed only by some kinds of constituents and not others. In the simplest case of a collection of matter without internal partitions, the regions of space $\boldsymbol{R}^A$ coincide at every time instant.

The amount n_i of the constituent in the i-th region of space can vary in time for two reasons:

- *matter exchange*: during a time interval in which the boundary surface of R_i is not entirely a wall, particles may be transferred into or out of R_i; we denote by $\dot{\boldsymbol{n}}^{A\leftarrow}$ the set of rates at which particles are transferred in or out of each region, assumed positive if inward, negative if outward;

- *reaction mechanisms*: in a portion of space where two or more regions overlap, the allowed reaction mechanisms may transform, according to well specified proportions (*e.g.*, stoichiometry), particles of one or more regions into particles of one or more other regions.

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 system A the set of all the compositions of A which are compatible with a given one. We will denote a set of compatible compositions for A by the symbol $(\boldsymbol{n}^{0A}, \boldsymbol{\nu}^A)$. By this we mean that the set of τ allowed reaction mechanisms is defined like for chemical reactions by a matrix of stoichiometric coefficients $\boldsymbol{\nu}^A = [\nu_k^{(\ell)}]$, with $\nu_k^{(\ell)}$ representing the stoichiometric coefficient of the k-th constituent in the ℓ-th reaction. The set of compatible compositions is a τ-parameter set defined by the reaction coordinates $\boldsymbol{\varepsilon}^A = \varepsilon_1^A, \ldots, \varepsilon_\ell^A, \ldots, \varepsilon_\tau^A$ through the proportionality relations

$$\boldsymbol{n}^A = \boldsymbol{n}^{0A} + \boldsymbol{\nu}^A \cdot \boldsymbol{\varepsilon}^A \ , \tag{1}$$

where $\boldsymbol{n}^{0A}$ denotes the composition corresponding to the value zero of all the reaction coordinates $\boldsymbol{\varepsilon}^A$. To fix ideas and for convenience, we will select $\boldsymbol{\varepsilon}^A = 0$ at time $t = 0$ so that $\boldsymbol{n}^{0A}$ is the composition at time $t = 0$ and we may call it the *initial composition.*

In general, the rate of change of the amounts of constituents is subject to the *amounts balance equations*

$$\dot{\boldsymbol{n}}^A = \dot{\boldsymbol{n}}^{A\leftarrow} + \boldsymbol{\nu}^A \cdot \dot{\boldsymbol{\varepsilon}}^A \ . \tag{2}$$

External force field. Let us denote by $\mathbf{F}$ a force field given by the superposition of a gravitational field $\mathbf{G}$, an electric field $\mathbf{E}$, and a magnetic induction field $\mathbf{B}$. Let us denote by Σ_t^A the union of all the regions of space $\boldsymbol{R}_t^A$ in which the constituents of C^A are contained, at a time instant t, which we also call region of space occupied by C^A at time t. Let us denote by Σ^A the union of the regions of space Σ_t^A, *i.e.*, the union of all the regions of space occupied by C^A during its time evolution.

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, $P_1^A, \ldots, P_n^A$, exists, such that when each P_i^A is applied on replicas of C^A at any given instant of time t: each replica responds with a numerical outcome which may vary from replica to replica; but either the time interval Δt employed to perform the measurement can be made arbitrarily short so that the measurement outcomes considered for P_i^A are those which correspond to the limit as $\Delta t \to 0$, or the measurement outcomes are independent of the time interval Δt employed to perform the measurement;

3. the arithmetic mean $\langle P_i^A \rangle_t$ of the numerical outcomes of repeated applications of any of these procedures, P_i^A, at an instant t, on an ensemble of

identically prepared replicas, is a value which is the same for every subensemble of replicas of $\mathcal{C}^A$ (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 $\mathcal{C}^A$ at time t;

4. the set of measurement procedures, $P_1^A, \ldots, P_n^A$, is *complete* in the sense that the set of values $\{\langle P_1^A \rangle_t, \ldots, \langle P_n^A \rangle_t\}$ allows to predict the value of any other measurement procedure satisfying conditions 2 and 3.

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

Comment. Although in general the amounts of constituents, $\boldsymbol{n}_t^A$, and the reaction rates, $\dot{\boldsymbol{\varepsilon}}_t$, are properties according to the above definition, we will list them separately and explicitly whenever it is convenient for clarity. In particular, in typical chemical kinetic models, $\dot{\boldsymbol{\varepsilon}}_t$ is assumed to be a function of $\boldsymbol{n}_t^A$ and other properties.

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, $\{\langle P_1 \rangle_t, \ldots, \langle P_n \rangle_t\}$,
- 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, $\mathbf{F}_{e,t}^A$.

With respect to the chosen complete set of properties, we can write

$$A_t \equiv \left\{ \langle P_1 \rangle_t, \ldots, \langle P_n \rangle_t; \boldsymbol{n}_t^A; \boldsymbol{R}_t^A; \dot{\boldsymbol{n}}_t^{A\leftarrow}; \mathbf{F}_{e,t}^A \right\} \quad . \qquad (3)$$

For shorthand, states A_{t_1}, A_{t_2},..., are denoted by A_1, A_2,.... Also, when the context allows it, the value $\langle P^A \rangle_{t_1}$ of property P^A of system A at time t_1 is denoted depending on convenience by the symbol P_1^A, or simply P_1.

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. Given a system C in the external force field $\mathbf{F}_e^C$, we will say that C is the *composite* of systems A and B, denoted AB, if: (a) there exists a pair of systems A and B such that the external force field which obtains when both A and B are removed and placed far away coincides with $\mathbf{F}_e^C$; (b) no region of space R_i^A overlaps with any region of space R_j^B; and (c) the $r_C = r_A + r_B$ regions of space of C are $\boldsymbol{R}^C = R_1^A, \ldots, R_i^A, \ldots, R_{r_A}^A, R_1^B, \ldots, R_j^B, \ldots, R_{r_B}^B$. Then we say that A and B are *subsystems* of the *composite system* C, and 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) only the particles of I are present in Σ^I; (b) the external force field for I, $\mathbf{F}_e^I$, is stationary, *i.e.*, time independent and conservative.

Comment. In simpler words, a system I is isolated if, at every time instant: no other material particle is present in the whole region of space Σ^I which will be crossed by system I during its time evolution; if system I is removed, only a stationary (vanishing or non-vanishing) conservative force field is present in Σ^I.

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:

- 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.

Subsystems in uncorrelated states. 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, at time t, we say that the states of subsystems A and B are *uncorrelated from each other*, and we write the state of AB as $(AB)_t = A_t B_t$. We also say, for brevity, that A and B are *systems uncorrelated from each other* at time t.

Correlated states, correlation. If at time t the states A_t and B_t do not fully determine the state $(AB)_t$ of the composite system AB, we say that A_t and B_t are *states correlated with each other.* We also say, for brevity, that A and B are *systems correlated with each other* at time t.

Comment. Two systems A and B which are uncorrelated from each other at time t_1 can undergo an interaction such that they are correlated with each other at time $t_2 > t_1$.

Comment. Correlations between isolated systems. Let us consider an isolated system $I = AB$ such that, at time t, system A is separable and uncorrelated from B. This circumstance does not exclude that, at time t, A and/or B (or both) may be correlated with a system C, even if the latter is isolated, *e.g.* it is far away from the region of space occupied by AB. Indeed our definitions of separability and correlation are general enough to be fully compatible with the notion of quantum correlations, *i.e.*, *entanglement*, which plays an important role in modern physics. In other words, assume that an isolated system U is made of three subsystems A, B, and C, *i.e.*, $U = ABC$, with C isolated and AB isolated. The fact that A is uncorrelated from B, so that according to our notation we may write $(AB)_t = A_t B_t$, does not exclude that A and C may be entangled, in such a way that the states A_t and C_t do not determine the state of AC, *i.e.*, $(AC)_t \neq A_t C_t$, *nor* we can write $U_t = (A)_t(BC)_t$.

Environment of a system, scenario. If for the time span of interest 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 will 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; thus all the remaining systems in the universe, even if correlated with AB, are considered as not available for interaction.

Comment. A system uncorrelated from its environment in one scenario, may be correlated with its environment in a broader scenario. Consider a system A which, in the scenario AB, is uncorrelated from its environment B at time t. If at time t system A is entangled with an isolated system C, in the scenario ABC, A is correlated with its environment BC.

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. We call *cycle* for a system A a process whereby the final state A_2 coincides with the initial state A_1.

Comment. In every process of any system A, the force field $\mathbf{F}_e^{AB}$ external to AB, where B is the environment of A, cannot change. In fact, AB is an isolated system and, as a consequence, the force field external to AB is stationary. Thus, in particular, for all the states in which a system A is separable:

- the force field $\mathbf{F}_e^{AB}$ external to AB, where B is the environment of A, is the same;
- the force field $\mathbf{F}_e^{A}$ external to A coincides, where defined, with the force field $\mathbf{F}_e^{AB}$ external to AB, *i.e.*, the force field produced by B (if any) has no effect on A.

Process between uncorrelated states, external effects. A process in the scenario AB in which the end states of system A are both uncorrelated from its environment B is called *process between uncorrelated states* and denoted by $\Pi_{12}^{A,B} \equiv (A_1 \to A_2)_{B_1 \to B_2}$. In such a process, the change of state of the environment B from B_1 to B_2 is called *effect external to A*. Traditional expositions of thermodynamics consider only this kind of process.

Composite process. A time-ordered sequence of processes between uncorrelated states of a system A with environment B, $\Pi_{1k}^{A,B} = (\Pi_{12}^{A,B}, \Pi_{23}^{A,B}, \ldots, \Pi_{(i-1)i}^{A,B}, \ldots, \Pi_{(k-1)k}^{A,B})$ is called a *composite process* if the final state of AB for process $\Pi_{(i-1)i}^{A,B}$ is the initial state of AB for process $\Pi_{i(i+1)}^{A,B}$, for $i = 1, 2, \ldots, k-1$. When the context allows the simplified notation Π_i for $i = 1, 2, \ldots, k-1$ for the processes in the sequence, the *composite process* may also be denoted by $(\Pi_1, \Pi_2, \ldots, \Pi_i, \ldots, \Pi_{k-1})$.

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 $(AB)_1 \to (AB)_2$. With different words, a process of an isolated system $I = AB$ is reversible if it can be reproduced as a part of a cycle of the isolated system I. For a reversible process between uncorrelated states, $\Pi_{12}^{A,B} \equiv (A_1 \to A_2)_{B_1 \to B_2}$, the *reverse* will be denoted by $-\Pi_{12}^{A,B} \equiv (A_2 \to A_1)_{B_2 \to B_1}$.

Comment. The reverse process may be achieved in more than one way (in particular, not necessarily by retracing the sequence of states $(AB)_t$, with $t_1 \le t \le t_2$, followed by the isolated system AB during the forward process).

Comment. The reversibility in one scenario does not grant the reversibility in another. If the smallest isolated system which contains A is AB and another isolated system C exists in a different region of space, one can choose as environment of A either B or BC. Thus, the time evolution of A can be described by the process $(AB)_1 \to (AB)_2$ in the scenario AB or by the process $(ABC)_1 \to (ABC)_2$ in the scenario ABC. For instance, the process $(AB)_1 \to (AB)_2$ could be irreversible, however by broadening the scenario so that interactions between AB and C become available, a reverse process $(ABC)_2 \to (ABC)_1$ may be possible. On the other hand, a process $(ABC)_1 \to (ABC)_2$ could be irreversible on account of an irreversible evolution $C_1 \to C_2$ of C, even if the process $(AB)_1 \to (AB)_2$ is reversible.

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. Actually, as well represented in [17] and clearly understood within dynamical systems models based on linear or nonlinear master equations, the time evolution of the state of a system is the result of a competition between (hamiltonian) mechanisms which are reversible and (dissipative) mechanisms which are not. So, to design a reversible process in the nonequilibrium domain, we most likely need a *fast* process, whereby the state is changed quickly by a fast hamiltonian dynamics, leaving negligible time for the dissipative mechanisms to produce irreversible effects.

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

- M is closed, it has a single constituent contained in a single region of space whose shape and volume are fixed,
- it has a constant mass m;
- 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 is identified by the unit vector $\mathbf{k} = \nabla z$;
- along the straight line there is a uniform stationary external gravitational force field $\mathbf{G}_e = -g\mathbf{k}$, where g is a constant gravitational acceleration.

As a consequence, the difference in potential energy between any initial and final states of M is given by $mg(z_2 - z_1)$.

Weight process, work in a weight process. A process between states of a closed system A in which A is separable and uncorrelated from its environment 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. We call *work performed by A (or, done by A) in the weight process*, denoted by the symbol $W_{12}^{A\rightarrow}$, the quantity

$$W_{12}^{A\rightarrow} = mg(z_2 - z_1) \ . \tag{4}$$

Clearly, the *work done by A* is positive if $z_2 > z_1$ and negative if $z_2 < z_1$. Two equivalent symbols for the opposite of this work, called *work received by A*, are $-W_{12}^{A\rightarrow} = W_{12}^{A\leftarrow}$.

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

- A is a separable system at time t;
- 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, where defined, with $\mathbf{F}_e^{AB}$.

Stable equilibrium state of a closed system. 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.

Comment. The stability of equilibrium in one scenario does not grant the stability of equilibrium in another. Consider a system A which, in the scenario AB, is uncorrelated from its environment B at time t and is in a stable equilibrium state. If at time t system A is entangled with an isolated system C, then in the scenario ABC, A is correlated with its environment BC, therefore, our definition of stable equilibrium state is not satisfied.

IV. DEFINITION OF ENERGY FOR A CLOSED SYSTEM

First Law. Every pair of states (A_1, A_2) of a closed system A in which A is separable and uncorrelated from its environment 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 closed system A in which A is separable and uncorrelated from its environment. 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:

$$E_2^A - E_1^A = W_{12}^{A\leftarrow} \quad \text{or} \quad E_2^A - E_1^A = W_{21}^{A\rightarrow} . \tag{5}$$

The first law guarantees that at least one of the weight processes considered in Eq. (5) 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. (5) yield the same result ($W_{12}^{A\leftarrow} = W_{21}^{A\rightarrow}$);
(b) the energy difference between two states A_2 and A_1 in which A is separable and uncorrelated from its environment depends only on the states A_1 and A_2;
(c) (*additivity of energy differences for separable systems uncorrelated from each other*) consider a pair of closed systems A and B; if A_1B_1 and A_2B_2 are states of the composite system AB such that AB is separable and uncorrelated from its environment and, in addition, A and B are separable and uncorrelated from each other, then

$$E_2^{AB} - E_1^{AB} = E_2^A - E_1^A + E_2^B - E_1^B \ ; \tag{6}$$

(d) (*energy is a property for every separable system uncorrelated from its environment*) let A_0 be a reference state of a closed system A in which A is separable and uncorrelated 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 and uncorrelated from its environment is determined uniquely by the equation

$$E_1^A = E_0^A + W_{01}^{A\leftarrow} \quad \text{or} \quad E_1^A = E_0^A + W_{10}^{A\rightarrow} \tag{7}$$

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; therefore, energy is a property of A.
Rigorous proofs of these consequences can be found in [17, 36], and will not be repeated here. In the proof of Eq. (6), the restrictive condition of the absence of correlations between AB and its environment as well as between A and B, implicit in [17] and [36], can be released by means of an assumption (Assumption 3) which is presented and discussed in the next section. As a result, Eq. (6) holds also if $(AB)_1$ e $(AB)_2$ are arbitrarily chosen states of the composite system AB, provided that AB, A and B are separable systems.

V. DEFINITION OF THERMODYNAMIC ENTROPY FOR A CLOSED SYSTEM

Assumption 1: restriction to normal system. We will call *normal system* any system A that, starting from every state in which it is separable and uncorrelated from its environment, 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 change (and A is again separable and uncorrelated from its environment).

From here on, we consider only normal systems; even when we say only *system* we mean a *normal system.*

Comment. For a normal system, the energy is unbounded from above; the system can accommodate an indefinite amount of energy, such as when its constituents have translational, rotational or vibrational degrees of freedom. 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. Notable exceptions to this assumption are important quantum theoretical model systems, such as spins, qubits, qudits, etc. whose energy is bounded from above. The extension of our treatment to such so-called *special systems* is straightforward, but we omit it here for simplicity.

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. 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 composite process (Π_1, Π_2) would violate the definition of stable equilibrium state.

Comment. Kelvin-Planck statement of the Second Law. As noted in [21] and [17, p.64], the impossibility of a perpetual motion machine of the second kind (PMM2), which is also known as the *Kelvin-Planck statement of the Second Law*, is a corollary of the definition of stable equilibrium state, provided that we adopt the (usually implicitly) restriction to normal systems (Assumption 1).

Second Law. Among all the states in which a closed system A is separable and uncorrelated from its environment and 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.

Comment. Statements of the Second Law. The combination of our statement of the Second Law and Lemma 1 establishes, for a closed system whose matter is constrained into given regions of space, the existence and uniqueness of a stable equilibrium state for every value of the energy; this proposition is known as the *Hatsopoulos-Keenan statement of the Second Law* [21]. Well-known historical statements of the Second Law, in addition to the Kelvin-Planck statement discussed above, are due to Clausius and to Carathéodory. In [17, p.64, p.121, p.133] it is shown that each of these historical statements is a logical consequence of the Hatsopoulos-Keenan statement combined with a further assumption, essentially equivalent to our Assumption 2 below.

Lemma 2. Any stable equilibrium state A_s 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 and uncorrelated with its environment and has 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.

Corollary 1. Any state in which a closed system A is separable and uncorrelated 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 the Second Law, Lemma 1 and Lemma 2.

Mutual stable equilibrium states. We say that two stable equilibrium states $A_{\rm se}$ and $B_{\rm se}$ are *mutual stable equilibrium states* if, when A is in state $A_{\rm se}$ and B in state $B_{\rm se}$, the composite system AB is in a stable equilibrium state. The definition holds also for a pair of states of the same system: in this case, system AB is composed of A and of a duplicate of A.

Identical copy of a system. We say that a system A^d, always separable from A and uncorrelated with A, is an *identical copy* of system A (or, a *duplicate* of A) if, at every time instant:

- the difference between the set of regions of space $\boldsymbol{R}^{A^d}$ occupied by the matter of A^d and that $\boldsymbol{R}^A$ occupied by the matter of A is only a rigid translation $\Delta\mathbf{r}$ with respect to the reference frame considered, and the composition of A^d is compatible with that of A;
- the external force field for A^d at any position $\mathbf{r}+\Delta\mathbf{r}$ coincides with the external force field for A at the position $\mathbf{r}$.

Thermal reservoir. We call *thermal reservoir* a 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 such that in any of its stable equilibrium states, R is in mutual stable equilibrium with an identical copy of R, R^d, in any of its 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 [17, 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.

Reference thermal reservoir. A thermal reservoir chosen once and for all, will be called a *reference thermal reservoir.* To fix ideas, we will choose as our reference thermal reservoir one having water as constituent, with a volume, an amount, and a range of energy values which correspond to the so-called *solid-liquid-vapor triple-point* stable equilibrium states.

Standard weight process. Given a pair of states (A_1, A_2) of a closed system A, in which A is separable and uncorrelated from its environment, 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) in which a closed system A is separable and uncorrelated from its environment can be interconnected by a reversible standard weight process for AR, where R is an arbitrarily chosen thermal reservoir.

Theorem 2. For a given closed 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) in which system A is separable and uncorrelated from its environment, 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 1, 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 by R_2 the initial and the final states of R in process $\Pi_{AR\rm rev}$. Let us denote by R^d the duplicate of R which is employed in process Π_{AR}, by R^d_3 and by R^d_4 the initial and the final states of R^d in this process. Let us suppose, *ab absurdo*, that $(\Delta E^R)^{\rm swrev}_{A_1A_2} > (\Delta E^R)^{\rm sw}_{A_1A_2}$. Then, the composite process $(-\Pi_{AR\rm rev}, \Pi_{AR})$ 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 change, in contrast with Theorem 1. Therefore, $(\Delta E^R)^{\rm swrev}_{A_1A_2} \le (\Delta E^R)^{\rm sw}_{A_1A_2}$.
Proof of b). If Π_{AR} is reversible too, then, in addition to $(\Delta E^R)^{\rm swrev}_{A_1A_2} \le (\Delta E^R)^{\rm sw}_{A_1A_2}$, the relation $(\Delta E^R)^{\rm sw}_{A_1A_2} \le$

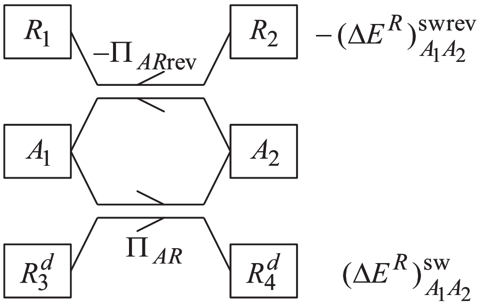

FIG. 1: Illustration of the proof of Theorem 2: standard weight processes $\Pi_{AR\mathrm{rev}}$ (reversible) and Π_{AR}; R^d is a duplicate of R; see text.

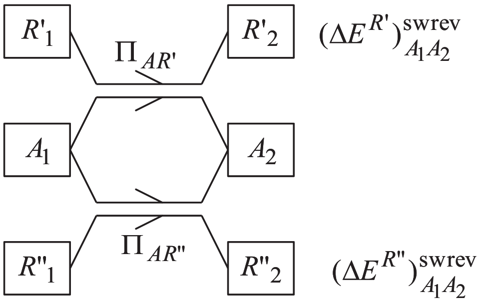

FIG. 2: Illustration of the proof of Theorem 3, part a): reversible standard weight processes $\Pi_{AR'}$ and $\Pi_{AR''}$, see text.

$(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2}$ must hold too. Otherwise, the composite process ($\Pi_{AR\mathrm{rev}}$, $-\Pi_{AR}$) would be a weight process for RR^d in which, starting from the stable equilibrium state $R_1R_4^d$, the energy of RR^d is lowered and the regions of space occupied by the constituents of RR^d have no net change, in contrast with Theorem 1. Therefore, $(\Delta E^R)^{\mathrm{swrev}}_{A_1A_2} = (\Delta E^R)^{\mathrm{sw}}_{A_1A_2}$.

Proof of c). Let Π_{AR} be a standard weight process for AR, from A_1 to A_2, such that $(\Delta E^R)^{\mathrm{sw}}_{A_1A_2} = (\Delta E^R)^{\mathrm{swrev}}_{A_1A_2}$, and let R_1 be the initial state of R in this process. Let $\Pi_{AR\mathrm{rev}}$ 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_3^d coincides with R_1 and R_4^d coincides with R_2. The composite process (Π_{AR}, $-\Pi_{AR\mathrm{rev}}$) 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, $(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2}$ and $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}$ respectively, in the reversible standard weight processes $\Pi_{AR'} = (A_1R'_1 \to A_2R'_2)^{\mathrm{swrev}}$ and $\Pi_{AR''} = (A_1R''_1 \to A_2R''_2)^{\mathrm{swrev}}$, where ($A_1$, A_2) is an arbitrarily chosen pair of states of any closed system A in which A is separable and uncorrelated from its environment. Then the ratio $(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2}/(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}$:

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 2, let us suppose that $(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2} < 0$. Then, $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}$ 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 region of space occupied by R' has no net change, in contrast with Theorem 1. Moreover, $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}$ 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

$$W^{R'R''\to} = -(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2} + (\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2} \ , \qquad (8)$$

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 $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}$ 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 change, in contrast with Theorem 1. Therefore, the assumption $(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2} < 0$ implies $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2} < 0$.

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

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

With the help of Figure 3, we will prove that the changes in energy of the reservoirs in these processes obey the relation

$$\frac{(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2}}{(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2}} = \frac{(\Delta E^{R'})^{\mathrm{swrev}}_{A'_1A'_2}}{(\Delta E^{R''})^{\mathrm{swrev}}_{A'_1A'_2}} \ . \qquad (9)$$

Let us assume: $(\Delta E^{R'})^{\mathrm{swrev}}_{A_1A_2} > 0$ and $(\Delta E^{R'})^{\mathrm{swrev}}_{A'_1A'_2} > 0$, which implies, $(\Delta E^{R''})^{\mathrm{swrev}}_{A_1A_2} > 0$ and $(\Delta E^{R''})^{\mathrm{swrev}}_{A'_1A'_2} > 0$ on account of part a) of the proof. 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 an arbitrarily high accuracy

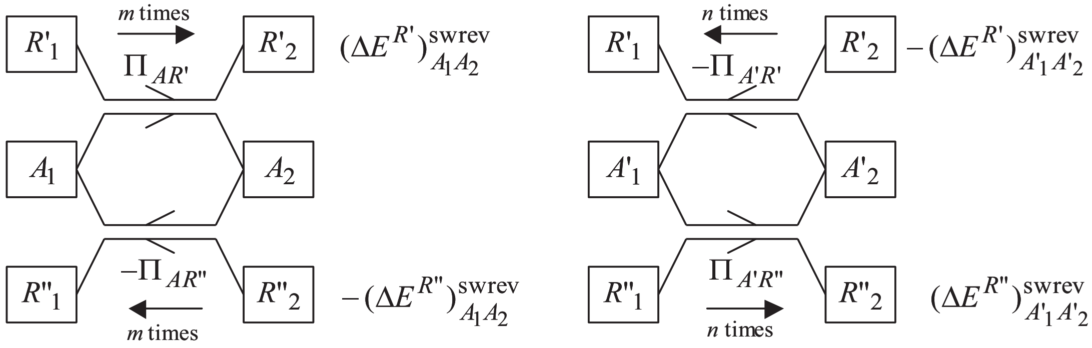

FIG. 3: Illustration of the proof of Theorem 3, part b): composite processes Π_A and $\Pi_{A'}$, see text.

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.*,

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

Therefore, as sketched in Figure 3, let us consider the composite processes Π_A and Π'_A defined as follows. Π_A is the following composite weight process for 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 processes for system $A'R'R''$ whereby starting from the end states of R' and R'' reached by 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 $(\Delta E^{R'})^{\rm swrev}_{A_1A_2}$ regardless of its initial state, and in each process $-\Pi_{A'R'}$ the energy change of R' is equal to $-(\Delta E^{R'})^{\rm swrev}_{A'_1A'_2}$. Therefore, the energy change of R' in the composite process $(\Pi_A,\, \Pi'_A)$ 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. (10). As a result, after $(\Pi_A,\, \Pi'_A)$, reservoir R' has been restored to its initial state, so that $(\Pi_A,\, \Pi'_A)$ is a reversible weight process for R''.

Again on account of Theorem 2, the overall energy change of R'' in $(\Pi_A,\, \Pi'_A)$ 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.*,

$$m\,(\Delta E^{R''})^{\rm swrev}_{A_1A_2} = n\,(\Delta E^{R''})^{\rm swrev}_{A'_1A'_2}\ . \tag{11}$$

Finally, taking the ratio of Eqs. (10) and (11), we obtain Eq. (9) 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 $(A_1,\, A_2)$ in which an arbitrary closed system A is separable and uncorrelated from its environment, 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

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

where T_{R^o} is a positive constant associated arbitrarily with the reference thermal reservoir R^o. If for R^o we select a thermal reservoir having water as constituent, with energy restricted to the solid-liquid-vapor triple-point range, and we set $T_{R^o} = 273.16$ K, we obtain the unit kelvin (K) for the thermodynamic temperature, which is adopted in the International System of Units (SI). Clearly, the temperature T_R of R is defined only up to an arbitrary multiplicative constant.

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

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

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 but otherwise arbitrary pair of states

$(A_1,\, A_2)$ in which a closed system A is separable and uncorrelated from its environment.

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. (12) we have

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

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

therefore the ratio of Eqs. (14) and (15) yields Eq. (13).

Corollary 3. Let $(A_1,\, A_2)$ be any pair of states in which a closed system A is separable and uncorrelated from its environment, and let $(\Delta E^{R})^{\rm swrev}_{A_1A_2}$ 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 $(\Delta E^{R})^{\rm swrev}_{A_1A_2}/T_R$ 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 (13) yields

$$\frac{(\Delta E^{R'})^{\rm swrev}_{A_1A_2}}{T_{R'}} = \frac{(\Delta E^{R''})^{\rm swrev}_{A_1A_2}}{T_{R''}}\ . \tag{16}$$

Definition of (thermodynamic) entropy for a closed system. Proof that it is a property. Let $(A_1\,,\, A_2)$ be any pair of states in which a closed system A is separable and uncorrelated from its environment B, and let R be an arbitrarily chosen thermal reservoir placed in B. We call *entropy difference* between A_2 and A_1 the quantity

$$S^A_2 - S^A_1 = -\frac{(\Delta E^{R})^{\rm swrev}_{A_1A_2}}{T_R} \tag{17}$$

where $(\Delta E^{R})^{\rm swrev}_{A_1A_2}$ 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 3, the right hand side of Eq. (17) is determined uniquely by states A_1 and A_2.

Let A_0 be a reference state in which A is separable and uncorrelated from its environment, 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 in which A is separable and uncorrelated from its environment, is determined uniquely by the equation

$$S^A_1 = S^A_0 - \frac{(\Delta E^{R})^{\rm swrev}_{A_1A_0}}{T_R}\ , \tag{18}$$

where $(\Delta E^{R})^{\rm swrev}_{A_1A_0}$ 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. Therefore, entropy is a property of A and is defined for every state of A in which A is separable and uncorrelated from its environment.

Theorem 4. Additivity of entropy differences for uncorrelated states. Consider the pairs of states $(C_1 = A_1B_1, C_2 = A_2B_2)$ in which the composite system $C = AB$ is separable and uncorrelated from its environment, and systems A and B are separable and uncorrelated from each other. Then,

$$S^{AB}_{A_2B_2} - S^{AB}_{A_1B_1} = S^A_2 - S^A_1 + S^B_2 - S^B_1\ . \tag{19}$$

Proof. Let us choose a thermal reservoir R, with temperature T_R, and consider the composite process $(\Pi_{AR},\, \Pi_{BR})$ 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 $(\Pi_{AR},\, \Pi_{BR})$ 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:

$$\frac{(\Delta E^{R})^{\rm swrev}_{C_1C_2}}{T_R} = \frac{(\Delta E^{R})^{\rm swrev}_{A_1A_2}}{T_R} + \frac{(\Delta E^{R})^{\rm swrev}_{B_1B_2}}{T_R}\ . \tag{20}$$

Equation (20) and the definition of entropy (17) yield Eq. (19).

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. Note, however, that the proof of additivity requires that (A_1, B_1) and (A_2, B_2) are pairs of states such that the subsystems A and B are uncorrelated from each other.

Theorem 5. Let $(A_1,\, A_2)$ be any pair of states in which a closed system A is separable and uncorrelated from its environment 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

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

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,

$$(\Delta E^{R})^{\rm swrev}_{A_1A_2} < (\Delta E^{R})^{\rm swirr}_{A_1A_2}\ . \tag{22}$$

Since T_R is positive, from Eqs. (22) and (17) one obtains

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

Theorem 6. Principle of entropy nondecrease. Let (A_1, A_2) be a pair of states in which a closed system A is separable and uncorrelated from its environment 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, $(\Delta E^R)^{\text{swrev}}_{A_1A_2} = 0$ and by applying the definition of entropy, Eq. (17), one obtains

$$S_2^A - S_1^A = -\frac{(\Delta E^R)^{\text{swrev}}_{A_1A_2}}{T_R} = 0 \ . \tag{24}$$

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, $(\Delta E^R)^{\text{swirr}}_{A_1A_2} = 0$ and Equation (21) yields

$$S_2^A - S_1^A > -\frac{(\Delta E^R)^{\text{swirr}}_{A_1A_2}}{T_R} = 0 \ . \tag{25}$$

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 $S_2^A - S_1^A = 0$.

Corollary 4. If states A_1 and A_2 can be interconnected by means of a reversible weight process for A, they have the same entropy. If states A_1 and A_2 can be interconnected by means of a zero-work reversible weight process for A, they have the same energy and the same entropy.

Proof. These are straightforward consequences of Theorem 6 together with the definition of energy.

Theorem 7. Highest-entropy principle. Among all the states of a closed system A such that A is separable and uncorrelated from its environment, the constituents of A are contained in a given set of regions of space $\boldsymbol{R}^A$ and the value of the energy E^A of A is fixed, the entropy of A has the highest value only in the unique stable equilibrium state A_{se} determined by $\boldsymbol{R}^A$ and E^A.

Proof. Let A_g be any other state of A in the set of states considered here. On account of the first law and of the definition of energy, A_g and A_{se} can be interconnected by a zero work weight process for A, either $(A_g \to A_{se})_W$ or $(A_{se} \to A_g)_W$. However, the existence of a zero work weight process $(A_{se} \to A_g)_W$ would violate the definition of stable equilibrium state. Therefore, a zero work weight process $(A_g \to A_{se})_W$ exists and is irreversible, so that Theorem 6 implies $S_{se}^A > S_g^A$.

Assumption 3. Existence of spontaneous decorrelations and impossibility of spontaneous creation of correlations. Consider a system AB composed of two closed subsystems A and B. Let $(AB)_1$ be a state in which AB is separable and uncorrelated from its environment and such that in the corresponding states A_1 and B_1, systems A and B are separable but correlated; let A_1B_1 be the state of AB such that the corresponding states A_1 and B_1 of A and B are the same as for state $(AB)_1$, but A and B are uncorrelated. Then, a zero work weight process $((AB)_1 \to A_1B_1)_W$ for AB is possible, while a weight process $(A_1B_1 \to (AB)_1)_W$ for AB is impossible.

Corollary 5. Energy difference between states of a composite system in which subsystems are correlated with each other. Let $(AB)_1$ and $(AB)_2$ be states of a composite system AB in which AB is separable and uncorrelated from its environment, while systems A and B are separable but correlated with each other. We have

$$\begin{aligned} E^{AB}_{(AB)_2} - E^{AB}_{(AB)_1} &= E^{AB}_{A_2B_2} - E^{AB}_{A_1B_1} \\ &= E_2^A - E_1^A + E_2^B - E_1^B \ . \end{aligned} \tag{26}$$

Proof. Since a zero work weight process $((AB)_1 \to A_1B_1)_W$ for AB exists on account of Assumption 3, states $(AB)_1$ and A_1B_1 have the same energy. In other words, the energy of a composite system in state $(AB)_1$ with separable but correlated subsystems coincides with the energy of the composite system in state A_1B_1 where its separable subsystems are uncorrelated in the corresponding states A_1 and A_2.

Definition of energy for a state in which a system is correlated with its environment. On account of Eq. (26), we will say that the energy of a system A in a state A_1 in which A is correlated with its environment is equal to the energy of system A in the corresponding state A_1 in which A is uncorrelated from its environment.

Comment. Equation (26) and the definition of energy for a state in which a system is correlated with its environment extend the definition of energy and the proof of the additivity of energy differences presented in [17, 36] to the case in which systems A and B are separable but correlated with each other.

To our knowledge, Assumption 3 (never made explicit) underlies all reasonable models of relaxation and decoherence.

Corollary 6. De-correlation entropy. Given a pair of (different) states $(AB)_1$ and A_1B_1 as defined in Assumption 3, then we have

$$\sigma^{AB}_{(AB)_1} = S^{AB}_{A_1B_1} - S^{AB}_{(AB)_1} > 0 \ , \tag{27}$$

where the positive quantity σ_1^{AB} is called the *de-correlation entropy*[39] of state $(AB)_1$. Clearly, if the subsystems are uncorrelated, *i.e.*, if $(AB)_1 = A_1B_1$, then $\sigma^{AB}_{(AB)_1} = \sigma^{AB}_{A_1B_1} = 0$.

Proof. On account of Assumption 3, a zero work weight process $\Pi_{AB} = ((AB)_1 \to A_1B_1)_W$ for AB exists. Process Π_{AB} is irreversible, because the reversibility of Π_{AB}

would require the existence of a zero work weight process for AB from A_1B_1 to $(AB)_1$, which is excluded by Assumption 3. Since Π_{AB} is irreversible, Theorem 6 yields the conclusion.

Comment. Let $(AB)_1$ and $(AB)_2$ be a pair of states of a composite system AB such that AB is separable and uncorrelated from its environment, while subsystems A and B are separable but correlated with each other. Let A_1B_1 and A_2B_2 be the corresponding pairs of states of AB, in which the subsystems A and B are in the same states as before, but are uncorrelated from each other. Then, the entropy difference between $(AB)_2$ and $(AB)_1$ is not equal to the entropy difference between A_2B_2 and A_1B_1 and therefore, on account of Eq. (19), it is not equal to the sum of the entropy difference between A_2 and A_1 and the entropy difference between B_2 and B_1, evaluated in the corresponding states in which subsystems A and B are uncorrelated from each other. In fact, combining Eq. (19) with Eq. (27), we have

$$\begin{aligned} S^{AB}_{(AB)_2} - S^{AB}_{(AB)_1} \;=\; & (S^A_2 - S^A_1) + (S^B_2 - S^B_1) \\ & -(\sigma^{AB}_{(AB)_2} - \sigma^{AB}_{(AB)_1}) \;\; . \end{aligned} \tag{28}$$

VI. FUNDAMENTAL RELATION, TEMPERATURE, AND GIBBS RELATION FOR CLOSED SYSTEMS

Set of equivalent stable equilibrium states. We will call *set of equivalent stable equilibrium states* of a closed system A, denoted ESE^A, a subset of its stable equilibrium states such that any pair of states in the set:

- differ from one another by some geometrical features of the regions of space $\boldsymbol{R}^A$;
- have the same composition;
- can be interconnected by a zero-work reversible weight process for A and, hence, by Corollary 4, have the same energy and the same entropy.

Comment. Let us recall that, for all the stable equilibrium states of a closed system A in a scenario AB, system A is separable and the external force field $\mathbf{F}^A_e = \mathbf{F}^{AB}_e$ is the same; moreover, all the compositions of A belong to the same set of compatible compositions $(\boldsymbol{n}^{0A}, \nu^A)$.

Parameters of a closed system. We will call *parameters* of a closed system A, denoted by $\boldsymbol{\beta}^A = \beta^A_1, \ldots, \beta^A_s$, a minimal set of real variables sufficient to fully and uniquely parametrize all the different sets of equivalent stable equilibrium states ESE^A of A. In the following, we will consider systems with a finite number s of parameters.

Examples. Consider a system A consisting of a single particle confined in spherical region of space of volume V; the box is centered at position r which can move in a larger region where there are no external fields. Then, it is clear that any rotation or translation of the spherical box within the larger region can be effected in a zero-work weight process that does not alter the rest of the state. Therefore, the position of the center of the box is *not* a parameter of the system. The volume instead is a parameter. The same holds if the box is cubic. If it is a parallelepiped, instead, the parameters are the sides ℓ_1, ℓ_2, ℓ_3 but not its position and orientation. For a more complex geometry of the box, the parameters are any minimal set of geometrical features sufficient to fully describe its shape, regardless of its position and orientation. The same if instead of one, the box contains many particles.

Suppose now we have a spherical box, with one or many particles, that can be moved in a larger region where there are k subregions, each much larger than the box and each with an external electric field everywhere parallel to the x axis and with uniform magnitude E_{ek}. As part of the definition of the system, let us restrict it only to the states such that the box is fully contained in one of these regions. For this system, the magnitude of E_e can be changed in a weight process by moving A from one uniform field subregion to another, but this in general will vary the energy. Therefore, in addition to the volume of the sphere, this system will have k as a parameter identifying the subregion where the box is located. Equivalently, the subregion can be identified by the parameter E_e taking values in the set $\{E_{ek}\}$. For each value of the energy E, system A has a set ESE^A for every pair of values of the parameters $(V,\, E_e)$ with E_e in $\{E_{ek}\}$.

Corollary 7. Fundamental relation for the stable equilibrium states of a closed system. On the set of all the stable equilibrium states of a closed system A (in scenario AB, for given initial composition $\boldsymbol{n}^{0A}$, stoichiometric coefficients $\boldsymbol{\nu^A}$ and external force field $\mathbf{F}^A_e$), the entropy is given by a single valued function

$$S^A_{\rm se} = S^A_{\rm se}(E^A, \boldsymbol{\beta}^A) \;\; , \tag{29}$$

which is called *fundamental relation* for the stable equilibrium states of A. Moreover, also the reaction coordinates are given by a single valued function

$$\boldsymbol{\varepsilon}^A_{\rm se} = \boldsymbol{\varepsilon}^A_{\rm se}(E^A, \boldsymbol{\beta}^A) \;\; , \tag{30}$$

which specifies the unique composition compatible with the initial composition $\boldsymbol{n}^{0A}$, called the *chemical equilibrium composition.*

Proof. On account of the Second Law and Lemma 1, among all the states of a closed system A with energy E^A, the regions of space $\boldsymbol{R}^A$ identify a unique stable equilibrium state. This implies the existence of a single valued function $A_{\rm se} = A_{\rm se}(E^A, \boldsymbol{R}^A)$, where $A_{\rm se}$ denotes the state, in the sense of Eq. (3). By definition, for each value of the energy E^A, the values of the parameters $\boldsymbol{\beta}^A$ fully identify all the regions of space $\boldsymbol{R}^A$ that correspond to a set of equivalent stable equilibrium states ESE^A, which have the same value of the entropy and the same composition. Therefore, the values of E^A and $\boldsymbol{\beta}^A$ fix uniquely the values of $S^A_{\rm se}$ and of $\boldsymbol{\varepsilon}^A_{\rm se}$. This implies the existence of the single valued functions written in Eqs. (29) and (30).

Comment. Clearly, for a non-reactive closed system, the composition is fixed and equal to the initial, *i.e.*, $\boldsymbol{\varepsilon}^A_{\rm se}(E^A, \boldsymbol{\beta}^A) = 0$.
Usually [17, 21], in view of the equivalence that defines them, each set ESE^A is thought of as a single state called "a stable equilibrium state" of A. Thus, for a given closed system A (and, hence, given initial amounts of constituents), it is commonly stated that the energy and the parameters of A determine "a unique stable equilibrium state" of A, which is called "the chemical equilibrium state" of A if the system is reactive according to a given set of stoichiometric coefficients. For a discussion of the implications of Eq. (30) and its reduction to more familiar chemical equilibrium criteria in terms of chemical potentials see, *e.g.*, [7].

Assumption 4. The fundamental relation (29) is continuous and differentiable with respect to each of the variables E^A and $\boldsymbol{\beta}^A$.

Theorem 8. For any closed system, for fixed values of the parameters the fundamental relation (29) is a strictly increasing function of the energy.
Proof. Consider two stable equilibrium states $A_{\rm se1}$ and $A_{\rm se2}$ of a closed system A, with energies E^A_1 and E^A_2, entropies $S^A_{\rm se1}$ and $S^A_{\rm se2}$, and with the same regions of space occupied by the constituents of A (and therefore the same values of the parameters). Assume $E^A_2 > E^A_1$. By Assumption 1, we can start from state $A_{\rm se1}$ and, by a weight process for A in which the regions of space occupied by the constituents of A have no net changes, add work so that the system ends in a non-equilibrium state A_2 with energy E^A_2. By Theorem 6, we must have $S^A_2 \geq S^A_{\rm se1}$. Now, on account of Lemma 2, we can go from state A_2 to $A_{\rm se2}$ with a zero-work irreversible weight process for A. By Theorem 6, we must have $S^A_{\rm se2} > S^A_2$. Combining the two inequalities, we find that $E^A_2 > E^A_1$ implies $S^A_{\rm se2} > S^A_{\rm se1}$.

Corollary 8. The fundamental relation for any closed system A can be rewritten in the form

$$E^A_{\rm se} = E^A_{\rm se}(S^A, \boldsymbol{\beta}^A) \quad . \tag{31}$$

Proof. By Theorem 8, for fixed $\boldsymbol{\beta}^A$, Eq. (29) is a strictly increasing function of E^A. Therefore, it is invertible with respect to E^A and, as a consequence, can be written in the form (31).

Temperature of a closed system in a stable equilibrium state. Consider a stable equilibrium state $A_{\rm se}$ of a closed system A identified by the values of E^A and $\boldsymbol{\beta}^A$. The partial derivative of the fundamental relation (31) with respect to S^A, is denoted by

$$T^A = \left(\frac{\partial E^A_{\rm se}}{\partial S^A}\right)_{\boldsymbol{\beta}^A} \quad . \tag{32}$$

Such derivative is always defined on account of Assumption 45. When evaluated at the values of E^A and $\boldsymbol{\beta}^A$ that identify state $A_{\rm se}$, it yields a value that we call the *temperature* of state $A_{\rm se}$.

Comment. One can prove [17, p.127] that two stable equilibrium states A_1 and A_2 of a closed system A are mutual stable equilibrium states if and only if they have the same temperature, *i.e.*, if $T^A_1 = T^A_2$. Moreover, it is easily proved [17, p.136] that, when applied to a thermal reservoir R, Eq. (32) yields that all the stable equilibrium states of a thermal reservoir have the same temperature which is equal to the temperature T_R of R defined by Eq. (12).

Corollary 9. For any stable equilibrium state of any (normal) closed system, the temperature is non-negative.
Proof. The thesis follows immediately from the definition of temperature, Eq. (32), and Theorem 8.

Gibbs equation for a non-reactive closed system. By differentiating Eq. (31), one obtains (omitting the superscript "A" and the subscript "se" for simplicity)

$$dE = T\,dS + \sum_{j=1}^{s} F_j\,d\beta_j \quad , \tag{33}$$

where F_j is called generalized force conjugated to the j-th parameter of A, $F_j = \left(\partial E_{\rm se}/\partial\beta_j\right)_{S,\boldsymbol{\beta}'}$. If all the regions of space $\boldsymbol{R}^A$ coincide and the volume V of any of them is a parameter, the negative of the conjugated generalized force is called *pressure*, denoted by p, $p = -\left(\partial E_{\rm se}/\partial V\right)_{S,\boldsymbol{\beta}'}$.

Fundamental relation in the quantum formalism. Let us recall that the measurement procedures that define energy and entropy must be applied, in general, to a (homogeneous) ensemble of identically prepared replicas of the system of interest. Because the numerical outcomes may vary (fluctuate) from replica to replica, the values of the energy and the entropy defined by these procedures are arithmetic means. Therefore, what we have denoted so far, for simplicity, by the symbols E^A and S^A should be understood as $\langle E^A\rangle$ and $\langle S^A\rangle$. Where appropriate, like in the quantum formalism implementation, this more precise notation should be preferred. Then, written in full notation, the fundamental relation (29) for a closed system is

$$\langle S^A\rangle_{\rm se} = S^A_{\rm se}(\langle E^A\rangle, \boldsymbol{\beta}^A) \quad , \tag{34}$$

and the corresponding Gibbs relation

$$d\langle E\rangle = T\,d\langle S\rangle + \sum_{j=1}^{s} F_j\,d\beta_j \quad . \tag{35}$$

VII. DEFINITIONS OF ENERGY AND ENTROPY FOR AN OPEN SYSTEM

Our definition of energy is based on the First Law, by which a weight process is possible between any pair of states A_1 and A_2 in which a closed system A is separable and uncorrelated from its environment. Our definition of entropy is based on Assumption 2, by which a reversible standard weight process for AR is possible between any pair of states A_1 and A_2 in which a closed system A is separable and uncorrelated from its environment. In both cases, A_1 and A_2 have compatible compositions. In this section, we extend the definitions of energy and entropy to a set of states in which an open system O is separable and uncorrelated from its environment; two such states of O have, in general, non-compatible compositions.

Separable open system uncorrelated from its environment. Consider an open system O that has Q as its (open) environment, *i.e.*, the composite system OQ is isolated in $\mathbf{F}_e^{OQ}$. We say that system O is *separable* from Q at time t if the state $(OQ)_t$ of OQ can be reproduced as (*i.e.*, coincides with) a state $(AB)_t$ of an isolated system AB in $\mathbf{F}_e^{AB} = \mathbf{F}_e^{OQ}$ such that A and B are closed and separable at time t. If the state $(AB)_t = A_t B_t$, *i.e.*, is such that A and B are uncorrelated from each other, then we say that the open system O is *uncorrelated from its environment* at time t, and we have $O_t = A_t$, $Q_t = B_t$, and $(OQ)_t = O_t Q_t$.

Set of elemental species. Following [17, p.545], we will call *set of elemental species* a *complete* set of *independent* constituents with the following features: (1) (*completeness*) there exist reaction mechanisms by which all other constituents can be formed starting only from constituents in the set; and (2) (*independence*) there exist no reaction mechanisms that involve only constituents in the set.
For example, in chemical thermodynamics we form a set of elemental species by selecting among all the chemical species formed by atomic nuclei of a single kind those that have the most stable molecular structure and form of aggregation at standard temperature and pressure.

Energy and entropy of a separable open system uncorrelated from its environment. Let OQ be an isolated system in $\mathbf{F}_e^{OQ}$, with O and Q open systems, and let us choose scenario OQ, so that Q is the environment of O. Let us suppose that O has r single-constituent regions of space and a set of allowed reaction mechanisms with stoichiometric coefficients $\boldsymbol{\nu}^O$. Let us consider a state O_1 in which O is separable and uncorrelated from its environment and has composition $\boldsymbol{n}_1^O = (n_1^O, \ldots, n_i^O, \ldots, n_r^O)_1$. Let $A^{\boldsymbol{n}_1^O} B$ be an isolated system in $\mathbf{F}_e^{A^{\boldsymbol{n}_1^O} B} = \mathbf{F}_e^{OQ}$, such that $A^{\boldsymbol{n}_1^O}$ is closed, has the same allowed reaction mechanisms as O and compositions compatible with $\boldsymbol{n}_1^O$. Let $A_1^{\boldsymbol{n}_1^O}$ be a state of $A^{\boldsymbol{n}_1^O}$ such that, in that state, system $A^{\boldsymbol{n}_1^O}$ is a separable system in $\mathbf{F}_e^{A^{\boldsymbol{n}_1^O}} = \mathbf{F}_e^{A^{\boldsymbol{n}_1^O} B}$ and is uncorrelated from its environment; moreover, the state $A_1^{\boldsymbol{n}_1^O}$ coincides with O_1, *i.e.*, has the same values of all the properties. We will define as energy and entropy of O, in state O_1, the energy and the entropy of $A^{\boldsymbol{n}_1^O}$ in state $A_1^{\boldsymbol{n}_1^O}$, namely $E_1^O = E_1^{A^{\boldsymbol{n}_1^O}}$ and $S_1^O = S_1^{A^{\boldsymbol{n}_1^O}}$. The existence of system $A^{\boldsymbol{n}_1^O}$ and of state $A_1^{\boldsymbol{n}_1^O}$ is granted by the definition of separability for O in state O_1.

The values of the energy and of the entropy of $A^{\boldsymbol{n}_1^O}$, in state $A_1^{\boldsymbol{n}_1^O}$, are determined by choosing a reference state $A_0^{\boldsymbol{n}_1^O}$ of $A^{\boldsymbol{n}_1^O}$ and by applying Eqs. (7) and (18). The reference state $A_0^{\boldsymbol{n}_1^O}$ and the reference values $E_0^{A^{\boldsymbol{n}_1^O}}$ and $S_0^{A^{\boldsymbol{n}_1^O}}$ are selected as defined below.

We choose $A^{\boldsymbol{n}_1^O}$ as the composite of q closed subsystems, $A^{\boldsymbol{n}_1^O} = A^1 A^2 \cdots A^i \cdots A^q$, each one containing an elemental species, chosen so that the composition of $A^{\boldsymbol{n}_1^O}$ is compatible with that of O in state O_1. Each subsystem, A^i, contains n_i particles of the i-th elemental species and is constrained by a wall in a spherical box with a variable volume V^{A^i}; each box is very far from the others and is placed in a position where the external force field $\mathbf{F}_e^{A^{\boldsymbol{n}_1^O}}$ is vanishing.

We choose the reference state $A_0^{\boldsymbol{n}_1^O}$ to be such that each subsystem A^i is in a stable equilibrium state A_0^i with a prescribed temperature, T_0, and a volume $V_0^{A^i}$ such that the pressure has a prescribed value p_0.

We fix the reference values of the energy and the entropy of the reference state $A_0^{\boldsymbol{n}_1^O}$ as follows:

$$E_0^{A^{\boldsymbol{n}_1^O}} = \sum_{i=1}^{q} E_0^{A^i} \quad , \tag{36}$$

$$S_0^{A^{\boldsymbol{n}_1^O}} = \sum_{i=1}^{q} S_0^{A^i} \quad , \tag{37}$$

with the values of $E_0^{A^i}$ and $S_0^{A^i}$ fixed arbitrarily. Notice that by construction $V_0^{A^{\boldsymbol{n}_1^O}} = \sum_{i=1}^q V_0^{A^i}$ and, therefore, we also have $E_0^{A^{\boldsymbol{n}_1^O}} + p_0 V_0^{A^{\boldsymbol{n}_1^O}} = \sum_{i=1}^q (E_0^{A^i} + p_0 V_0^{A^i})$. In chemical thermodynamics, it is customary to set $E_0^{A^i} + p_0 V_0^{A^i} = 0$ and $S_0^{A^i} = 0$ for each elemental species.

Similarly to what seen for a closed system, the definition of energy for O can be extended to the states of O in which O is separable but correlated with its environment.

VIII. FUNDAMENTAL RELATION FOR AN OPEN SYSTEM

Stable equilibrium state of an open system. A state of an open system O in which O is a separable open system in $\mathbf{F}_e^O$ and is uncorrelated from its environment Q is called a stable equilibrium state if it can be reproduced as a stable equilibrium state of a closed system A in $\mathbf{F}_e^A = \mathbf{F}_e^O$.

We will consider separately the two different cases:
a) the constituents of O are non-reactive, *i.e.*, no reaction mechanism is allowed for O;
b) reactions with stoichiometric coefficients $\boldsymbol{\nu}^O$ are allowed for O.

Fundamental relation for the stable equilibrium states of an open system with non-reactive constituents. Let SE^O be the set of all the stable equilibrium states of an open system O with r non-reactive constituents and s parameters, $\boldsymbol{\beta}^O = \beta_1^O, \, \ldots \, , \beta_s^O$. Let us consider the subset $SE^O_{\boldsymbol{n}_1^O}$ of all the states of SE^O that have the composition $\boldsymbol{n}_1^O$, and let $A^{\boldsymbol{n}_1^O}$ be a closed system with composition $\boldsymbol{n}_1^O$, such that its stable equilibrium states coincide with those of the subset $SE^O_{\boldsymbol{n}_1^O}$ and therefore also the parameters coincide, *i.e.*, $\boldsymbol{\beta}^{A^{\boldsymbol{n}_1^O}} = \boldsymbol{\beta}^O$. Then, every subset $ESE^{A^{\boldsymbol{n}_1^O}}$ of equivalent stable equilibrium states of $A^{\boldsymbol{n}_1^O}$, which is determined by the energy $E^{A^{\boldsymbol{n}_1^O}}$ and the parameters $\boldsymbol{\beta}^{A^{\boldsymbol{n}_1^O}}$, coincides with a subset of equivalent stable equilibrium states of O with composition $\boldsymbol{n}_1^O$. The same argument can be repeated for every composition of O. Therefore, on the whole set SE^O, a relation with the form

$$S_{se}^O = S_{se}^O(E^O, \, \boldsymbol{n}^O, \, \boldsymbol{\beta}^O) \tag{38}$$

is defined and is called fundamental relation for O. Since the relation $S_{se}^O = S_{se}^O(E^O)$, for fixed values of $\boldsymbol{n}^O$ and $\boldsymbol{\beta}^O$, is strictly increasing, Eq. (38) can be rewritten as

$$E_{se}^O = E_{se}^O(S^O, \, \boldsymbol{n}^O, \, \boldsymbol{\beta}^O) \ \ . \tag{39}$$

Gibbs equation for a non-reactive open system. If the system has non-reactive constituents, the fundamental relation given by Eq. (39) applies. By differentiating Eq. (39), one obtains (omitting the superscript "O" and the subscript "se" for simplicity)

$$dE = TdS + \sum_{i=1}^{r} \mu_i \, \mathrm{d}n_i + \sum_{j=1}^{s} F_j \, \mathrm{d}\beta_j \ \ , \tag{40}$$

where μ_i is called the *total potential* of i-th constituent of O.
In Eq. (40), it is assumed that Eq. (39) is continuous and differentiable also with respect to $\boldsymbol{n}$. For systems with very large values of the amounts of constituents this condition is fulfilled. However, for very few particle closed systems, the variable $\boldsymbol{n}$ takes on only discrete values, and, according to our definition, a separable state of an open system must be reproduced as a separable state of a closed system. Thus, the extension of Eq. (40) to few particles open systems requires an *extended definition* of a separable state of an open system, which includes states with non integer numbers of particles. This extension will not be presented here.

Fundamental relation for the stable equilibrium states of an open system with reactive constituents. Let SE^O be the set of all the stable equilibrium states of an open system O with parameters $\boldsymbol{\beta}^O$ and constituents which can react according to a set of reaction mechanisms defined by the stoichiometric coefficients $\boldsymbol{\nu}^O$. Let $(\boldsymbol{n}_1^{0O}, \, \boldsymbol{\nu}^O)$ be the set of the compositions of O which are compatible with the initial composition $\boldsymbol{n}_1^{0O} = (n_1^{0O}, ..., n_r^{0O})_1$. Let $SE^{\boldsymbol{n}_1^{0O}}$ be the subset of SE^O with compositions compatible with $(\boldsymbol{n}_1^{0O}, \, \boldsymbol{\nu}^O)$ and let $A^{\boldsymbol{n}_1^{0O}}$ be a closed system with compositions compatible with $(\boldsymbol{n}_1^{0O}, \, \boldsymbol{\nu}^O)$ and stable equilibrium states that coincide with those of the subset $SE^{\boldsymbol{n}_1^{0O}}$ so that also the parameters coincide, *i.e.*, $\boldsymbol{\beta}^{A^{\boldsymbol{n}_1^{0O}}} = \boldsymbol{\beta}^O$.
Then, every subset $ESE^{A^{\boldsymbol{n}_1^{0O}}}$ of equivalent stable equilibrium states of $A^{\boldsymbol{n}_1^{0O}}$, which is determined by the energy $E^{A^{\boldsymbol{n}_1^{0O}}}$ and the parameters $\boldsymbol{\beta}^{A^{\boldsymbol{n}_1^{0O}}}$, coincides with a subset of equivalent stable equilibrium states in the set $SE^{\boldsymbol{n}_1^{0O}}$. The same argument can be repeated for every set of compatible compositions of O, $(\boldsymbol{n}_2^{0O}, \, \boldsymbol{\nu}^O)$, $(\boldsymbol{n}_3^{0O}, \, \boldsymbol{\nu}^O)$, etc. Therefore, on the whole set SE^O, the following single-valued relation is defined

$$S_{se}^O = S_{se}^O(E^O, \, \boldsymbol{n}^{0O}, \, \boldsymbol{\beta}^O) \tag{41}$$

which is called fundamental relation for O. Since the relation $S_{se}^O = S_{se}^O(E^O)$, for fixed values of $\boldsymbol{n}^{0O}$ and $\boldsymbol{\beta}^O$, is strictly increasing, Eq. (41) can be rewritten as

$$E_{se}^O = E_{se}^O(S^O, \, \boldsymbol{n}^{0O}, \, \boldsymbol{\beta}^O) \ \ . \tag{42}$$

Comment. On the set SE^O of the stable equilibrium states of O, also the reaction coordinates are given by a single valued function

$$\boldsymbol{\varepsilon}_{se}^O = \boldsymbol{\varepsilon}_{se}^O(E^O, \, \boldsymbol{n}^{0O}, \, \boldsymbol{\beta}^O) \ \ , \tag{43}$$

which defines the chemical equilibrium composition. The existence of Eq. (43) is a consequence of the existence of a single valued function such as Eq. (30) for each of the closed systems $A^{\boldsymbol{n}_1^{0O}}$, $A^{\boldsymbol{n}_2^{0O}}$, ... used to reproduce the stable equilibrium states of O with sets of amounts of constituents compatible with the initial compositions, $\boldsymbol{n}_1^{0O}$, $\boldsymbol{n}_2^{0O}$, etc.

IX. CONCLUSIONS

In this paper, a general definition of entropy is 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, environment of a system, process, separable system, system uncorrelated from its environment and parameters of a system are stated, which are valid also in the presence of internal semipermeable walls and reaction mechanisms. 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.

The role of correlations on the domain of definition and on the additivity of energy and entropy is discussed: it is proved that energy is defined for any separable system, even if correlated with its environment, and is additive for separable subsystems even if correlated with each other; entropy is defined only for a separable system uncorrelated from its environment and is additive only for separable subsystems uncorrelated from each other; the concept of decorrelation entropy is defined.

A definition of thermal reservoir less restrictive than in previous treatments is adopted: it is fulfilled, with an excellent approximation, 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 is completed by a new explicit proof that the entropy difference between two states of a system is independent of the initial state of the auxiliary thermal reservoir chosen to measure it.

The definition of a reversible process is 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 recent interpretations of irreversibility in the quantum mechanical framework.

Rigorous extensions of the definitions of energy and entropy to open systems are stated. The existence of a fundamental relation for the stable equilibrium states of an open system with reactive constituents is proved rigorously; it is shown that the amounts of constituents which correspond to given fixed values of the reaction coordinates should appear in this equation.

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