Rigorous and General Definition of Thermodynamic Entropy.
Part I: Basic Concepts and Energy

Enzo Zanchini[*] and Gian Paolo Beretta[†]

INTRODUCTION

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 [1] describes heat as one of several different forms of energy related to the jiggling motion of particles, a form of energy which really is just kinetic energy. Tisza [2] 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. Indeed, as pointed out by Hatsopoulos and Keenan [3], without the Second Law heat and work would be indistinguishable. Third, heat is a mode of energy transfer between systems that are very close to thermodynamic equilibrium, so that 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 [4] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim [5] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan [6] defines heat as that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. 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 [5]. However, Gyftopoulos and Beretta [7, 8] 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 Ref. [7], we will present and discuss a definition of entropy where the concept of heat is not employed.

Other problems are present in the traditional scheme for the definition of entropy [5, 6, 9]: many basic concepts, such as those of system, state, property, isolated system, environment of a system, adiabatic process are not defined rigorously; the unnecessary concept of *quasistatic process* is employed; it is assumed 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 this paper, a rigorous and general definition of entropy is presented, which is based on operative definitions of all the concepts employed and involves neither the concept of heat nor that of quasistatic process; it applies to both equilibrium and nonequilibrium states and considers also systems with movable internal walls and/or semipermeable walls, with chemical reactions and/or external force fields, with small numbers of particles. In Part I, the definitions of the basic concepts and of energy are presented. In part II, entropy and thermodynamic temperature are defined and the principle of entropy non-decrease is proved.

BASIC DEFINITIONS

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

Region of space which contains particles of the i-th constituent. We will call region of space which contains particles of the i-th constituent a connected region R_i of physical space (the three-dimensional Euclidean space) in which particles of the i-th constituent are contained. The boundary surface of R_i may be a patchwork

---

[*]Università di Bologna, Italy, enzo.zanchini@unibo.it
[†]Università di Brescia, Italy, beretta@ing.unibs.it

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 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.

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; reaction mechanisms.

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, $\boldsymbol{n}^{0A}$. We will denote a set of compatible compositions by the symbol $(\boldsymbol{n}^{0A}, \boldsymbol{\nu}^A)$, where $\boldsymbol{\nu}^A$ is the matrix of the stoichiometric coefficients.

External force field. Let us denote by $\mathbf{F}$ a force field given by the superposition of the gravitational field $\mathbf{G}$, the electric field $\mathbf{E}$ and the magnetic field $\mathbf{H}$. Let us denote by Σ_t^A the union of the regions of space R_t^A in which the constituents of C^A are contained, at a time instant t, which will also be called region of space occupied by C^A at time t. 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.

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, the arithmetic mean $\langle P_i^A \rangle_t$ of the numerical outcomes of repeated applications of P_i^A is a value which is the same for every subensemble of replicas of C^A (the latter condition guarantees the so-called statistical *homogeneity* of the ensemble); $\langle P_i^A \rangle_t$ is called the *value of P_i^A* for C^A at time t;
3. the set of measurement procedures, $P_1^A, \ldots, P_n^A$, 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.

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, $\mathbf{F}_{e,t}^A$.

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

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

Composite system, subsystems. If systems A and B, defined in the same time interval, are such that no region of space R_i^A overlaps with any region of space R_j^B, we will say that that the system C whose regions of

space of are $\boldsymbol{R}^C = R_1^A, \ldots, R_i^A, \ldots, R_{r_A}^A, R_1^B, \ldots, R_j^B, \ldots, R_{r_B}^B$ is the *composite* of systems A and B, and that A and B are *subsystems* of C. Then, we write $C = AB$ and denote its state at time t by $C_t = (AB)_t$.

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

Separable closed systems. Consider a composite system AB, with A and B closed subsystems. We say that systems A and B are *separable* at time t if:

- 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. $\mathbf{F}_{e,t}^B = \mathbf{F}_{e,t}^{AB}$.

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.

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

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

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

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

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

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

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

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

Weight process, work in a weight process. A process of a system A is called a *weight process*, denoted by $(A_1 \rightarrow A_2)_W$, 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 in the weight process*, denoted by the symbol $W_{12}^{A\rightarrow}$, the quantity

$$W_{12}^{A\rightarrow} = mg(z_2 - z_1) \ . \tag{1}$$

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

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

- state A_t does not change with time;
- state A_t can be reproduced while A is an isolated system in the external force field $\mathbf{F}_e^A$, which coincides with $\mathbf{F}_e^{AB}$.
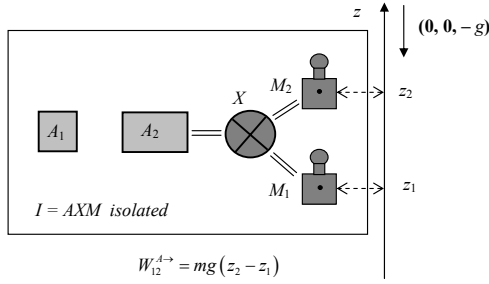
Figure 1: Schematic illustration of a weight process for system A.

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

DEFINITION OF ENERGY FOR A CLOSED SYSTEM

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

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

$$E_2^A - E_1^A = W_{12}^{A\leftarrow} \quad \text{or} \quad E_2^A - E_1^A = W_{21}^{A\rightarrow}. \tag{2}$$

The first law guarantees that at least one of the weight processes considered in Eq. 2 exists. Moreover, it yields the following consequences:

(a) if both weight processes $(A_1 \rightarrow A_2)_W$ and $(A_2 \rightarrow A_1)_W$ exist, the two forms of Eq. 2 yield the same result $(W_{12}^{A\leftarrow} = W_{21}^{A\rightarrow})$;

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

(c) (*additivity of energy differences*) consider a pair of states $A_1 B_1$ and $A_2 B_2$ of a composite system AB; then

$$E_2^{AB} - E_1^{AB} = E_2^A - E_1^A + E_2^B - E_1^B \ ; \tag{3}$$

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

$$E_1^A = E_0^A + W_{01}^{A\leftarrow} \quad \text{or} \quad E_1^A = E_0^A + W_{10}^{A\rightarrow} \tag{4}$$

where $W_{01}^{A\leftarrow}$ or $W_{10}^{A\rightarrow}$ is the work in any weight process for A either from A_0 to A_1 or from A_1 to A_0.

Rigorous proofs of these consequences can be found in Refs. [7, 10], and will not be repeated here.

References

[1] R. Feynmann, *Lectures on Physics*, Vol. 1, Addison-Welsey, 1963.

[2] L. Tisza, *Generalized Thermodynamics*, MIT Press, 1966, p. 16.

[3] G.N. Hatsopoulos and J.H. Keenan, *Principles of General Thermodynamics*, Wiley, 1965, p. xxiii.

[4] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Part I, 3rd Ed., Revised by E.M. Lifshitz and L.P. Pitaevskii, Translated by J.B. Sykes and M.J.Kearsley, Pergamon Press, 1980, p. 45.

[5] E.A. Guggenheim, *Thermodynamics*, North-Holland, 7th Ed., 1967, p. 10.

[6] J.H. Keenan, *Thermodynamics*, Wiley, 1941, p. 6.

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

[8] G.P. Beretta and E.P. Gyftopoulos, Teaching energy and entropy before temperature and heat, in *Proceedings of the 1991 Taormina Conference on Thermodynamics*, Accademia Peloritana dei Pericolanti, Messina, Vol. LXX-1, pp. 331-340 (1992); G.P. Beretta and E.P. Gyftopoulos, A novel sequence of exposition of engineering thermodynamics, in *Thermodynamics and the Design, Analysis, and Improvement of Energy Systems*, ASME Book AES-Vol. 30, HTD-Vol. 266, pp. 209-219 (1993).

[9] E. Fermi, *Thermodynamics*, Prentice-Hall, 1937.

[10] E. Zanchini, Thermodynamics: Energy of nonsimple systems and second postulate, *Il Nuovo Cimento B* **107 A**, pp. 123–139 (1992); E. Zanchini, On the definition of extensive property energy by the first postulate of thermodynamics, *Foundations of Physics* **16**, pp. 923–935 (1986).