Rigorous Axiomatic Definition of Entropy Valid Also for Non-Equilibrium States

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Abstract. We present a rigorous logical scheme for the definition of entropy, based on operative definitions of all the concepts employed, with all assumptions declared explicitly. Our treatment is an equivalent variation of the general definition of entropy given in E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics. Foundations and Applications*, Dover, Mineola, 2005. However, here we outline the minimal set of definitions and assumptions required to construct the same definition by the most direct and essential sequence of logical steps.

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.[1]

In our experience, however, when heat is introduced before the first law, and then used

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[1] For example, in his lectures on physics, Feynman [2] 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 [3] 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 first the student might find the idea of heat 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 [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. Similar definitions are adopted in many other notable textbooks that we have no space 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. It is one of the striking results of thermodynamics, that is, of the existence of entropy as a property of matter. Hatsopoulos and Keenan [7] have pointed out explicitly that, without the second law, heat and work would be indistinguishable and, therefore, a satisfactory definition of heat is unlikely without a prior statement of the second law.

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in the statement of the second law and in the definition of entropy, the student cannot avoid but sense ambiguity and lack of logical consistency. This results in the wrong but unfortunately widely spread conviction that thermodynamics is a confusing, ambiguous, hand-waving subject.[2]

In this paper, we summarize and illustrate the general definition of equilibrium and non-equilibrium entropy first given in Ref. [1]. The main reason why here we adopt a few variations, with respect to the exposition in Ref. [1], is to identify and clarify the minimal set of definitions and assumptions which provides the most direct and essential sequence of logical steps strictly necessary to construct such important and general definition. In view of the importance of non-equilibrium states for a wide range of applications of thermodynamics, we hope our paper helps to remove statements to the effect that entropy is defined only for equilibrium states from future textbooks.

BASIC DEFINITIONS

The term *system* in this paper is restricted for simplicity to mean *closed separable system*.[3] Due to space limitations, we omit here any discussion about the important definitions of property and state, which are available in Ref. [1].

A state of a system A is called *stationary* if it does not change in time. A stationary

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[2] During the past thirty years of teaching thermodynamics to undergraduate and graduate students from all over the globe, we have sensed a need for more clarity, unambiguity, generality and logical consistency in the exposition of thermodynamics than provided by traditional approaches. Continuing the effort pioneered by Keenan and Hatsopoulos, Ref. [1] provides the first complete answer to such long standing quest for going beyond the traditional Clausius definition of entropy in terms of heat.

The basic concepts and principles in Ref. [1] are introduced in a novel sequence that eliminates the problem of incomplete definitions, and that is valid for both macroscopic and microscopic systems (provided they are well defined, i.e., separable and uncorrelated from the rest of the universe), and for both equilibrium and non-equilibrium states. The laws of thermodynamics are presented as fundamental laws of physics that complement the laws of mechanics. In the statement of the first law, the definition of energy, the statement of the second law, the definition of entropy, and the concepts of energy and entropy exchanges between interacting systems, heat plays no role. It emerges only later in the logical development as a consequence of these concepts and laws, as a mode of energy exchange between systems that obtains under very restrictive conditions.

[3] Ref. [8] proposes a more precise definition than available in Ref. [1], as follows. We call *wall* a surface which cannot be crossed by material particles. A collection A of material particles is called a *closed system* if the particles are enclosed by walls in a region of space σ_A. A closed system may have also internal walls or semi-permeable walls. Let us denote by $\mathbf{G}$, $\mathbf{E}$ and $\mathbf{H}$ the gravitational, electric and magnetic fields, respectively, and by σ_{field} a region of space where a closed system A is contained. We call *external force field* for A, denoted by $\mathbf{G}_e$, $\mathbf{E}_e$, $\mathbf{H}_e$, the force field spatial distributions which are present in σ_{field} when system A is removed and placed far away from σ_{field}.

We say that I is an isolated system in the stationary force field $\mathbf{G}_e$, $\mathbf{E}_e$, $\mathbf{H}_e$—or simply, an *isolated system*—if only the particles of A are present in σ_{field} and the external force field $\mathbf{G}_e$, $\mathbf{E}_e$, $\mathbf{H}_e$ is stationary, i.e., time independent.

Consider an isolated system I in $\mathbf{G}_e$, $\mathbf{E}_e$, $\mathbf{H}_e$ and suppose that I can be subdivided into two closed systems A and B, such that the force fields experienced by the particles of A do not change if B is removed and placed far away from the region of space considered and the same holds for the particles of B when A is removed. Then, A and B are called *closed separable systems*, B is called the environment of A and A the environment of B.

state of A is called an *equilibrium state* if it can be reproduced while A is an isolated system. An equilibrium state that cannot be modified unless we change either the position of the walls which confine the matter of A or the state of the environment of A is called a *stable equilibrium state*. 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, the composite system AB is composed of A and of a duplicate of A.

We call *process* for A from state A_1 to state A_2, denoted $A_1 \to A_2$, the time evolution from A_1B_1 to A_2B_2 of AB, where B is the environment of A. A *cyclic process* or *cycle* for A is a process for A in which the initial and final states A_1 and A_2 coincide (even if states B_1 and B_2 are different).

A process for A is called a *weight process*, denoted $(A_1 \to A_2)_{\rm W}$, if the only effect in the environment of A is the change of state of a mechanical device M.[4] We call work performed by A in such a process, and denote it by $W_{12}^{A\to}$, the work done on M, i.e., $W_{12}^{A\to} = W_{12}^{M\leftarrow}$.

FIRST LAW AND ENERGY

First law. Every pair of states of any 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 property energy. Let $(A_1\ ,A_2)$ be any pair of states of A. We call *energy difference* between A_2 and A_1 either the opposite of the work performed by A in any weight process from A_1 to A_2 or the work performed by A in any weight process from A_2 to A_1; in symbols:

$$E(A_2) - E(A_1) = -W_{12}^{A\to} \quad \text{or} \quad E(A_2) - E(A_1) = W_{21}^{A\to}. \tag{1}$$

The first law guarantees that at least one of the weight processes considered in Eq. 1 exists. Moreover, it yields the following consequences: (*a*) if both weight processes $(A_1 \to A_2)_{\rm W}$ and $(A_2 \to A_1)_{\rm W}$ exist, the two forms of Eq. 1 yield the same result; (*b*) the energy difference between A_2 and A_1 depends only on the states A_1 and A_2, i.e., energy is a property of A; (*c*) if $C_1 = A_1B_1$ and $C_2 = A_2B_2$ are arbitrarily chosen states of a composite system $C = AB$, then

$$E(C_2) - E(C_1) = E(A_2) - E(A_1) + E(B_2) - E(B_1)\ . \tag{2}$$

Rigorous proofs of these consequences can be found in Refs. [1, 8, 9].

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[4] We call *mechanical device* a system M such that: (*a*) the state of M is determined uniquely by the position x of a material point P of M which can move along a straight line; (*b*) an external force $\mathbf{f}$ which depends only on x is applied to P. We denote by $W_{12}^{M\leftarrow}$ the work performed by the force $\mathbf{f}$ which acts on M while the position of P is changed from x_1 to x_2 , i.e., $W_{12}^{M\leftarrow} = \int_{x_1}^{x_2} f_x\ {\rm d}x$, where f_x is the component of $\mathbf{f}$ along the x direction.

SECOND LAW AND ENTROPY

Assumption 1. For every initial state of any system A, there exists a weight process for A such that: (a) the energy of A increases; (b) the region of space occupied by A in the final state is the same as in the initial state; and (c) the final state of A is a non-equilibrium state.

Assumption 2. Starting from any state, a system A can be changed to a stable equilibrium state by means of a zero-work weight process in which the region of space occupied by A has no net change.

We call *thermal reservoir* a system R which, for the regions of space and the range of energy values of interest, has stable equilibrium states that are all mutual equilibrium states. For example, water at the triple point obeys this definition.

We call *standard weight process* for AR a weight process for the composite system AR in which the end states of the thermal reservoir R are stable equilibrium states and the region of space occupied by R has no net change. We denote such process by $(A_1R_1 \rightarrow A_2R_2)_{\mathrm{sW}}$, and the energy change of the reservoir by $(\Delta E_R)^{\mathrm{sW}}_{A_1A_2}$.

Assumption 3. Every pair of states (A_1, A_2) of a system A can be interconnected by a reversible standard weight process for AR, where R is an arbitrarily chosen thermal reservoir.

Second law (for closed separable systems without internal partitions). Among all the states of a system A with a given value E of the energy and such that A is contained in a prescribed region of space σ_A, there exists a unique stable equilibrium state.

Theorem 1. *Impossibility of a PMM2*. If the initial state of A is a stable equilibrium state, it is impossible to lower the energy of A by means of a weight process for A in which the region of space σ_A occupied by A has no net change.

Theorem 2. Among all standard weight processes for AR between a given pair of states (A_1, A_2) of system A, the energy change $(\Delta E_R)^{\mathrm{sW}}_{A_1A_2}$ of the thermal reservoir R has a lower bound which is reached whenever the process is reversible.

Theorem 3. Let R' and R'' be any two thermal reservoirs and consider the energy changes, $(\Delta E_{R'})^{\mathrm{sW,rev}}_{A_1A_2}$ and $(\Delta E_{R''})^{\mathrm{sW,rev}}_{A_1A_2}$ respectively, in standard reversible weight processes $(A_1R'_1 \rightarrow A_2R'_2)^{\mathrm{rev}}_{\mathrm{sW}}$ and $(A_1R''_1 \rightarrow A_2R''_2)^{\mathrm{rev}}_{\mathrm{sW}}$, where ($A_1$, A_2) is an arbitrary pair of states of an arbitrary system A. Then the ratio $(\Delta E_{R'})^{\mathrm{sW,rev}}_{A_1A_2}$ / $(\Delta E_{R''})^{\mathrm{sW,rev}}_{A_1A_2}$ is positive and depends only on R' and R'', i.e., it is independent of *(a)* the initial stable equilibrium states of R' and R'', *(b)* the choice of system A, and *(c)* the choice of states A_1 and A_2.

Definition of temperature of a thermal reservoir. Let R be a given thermal reservoir and R^o a reference thermal reservoir. Select an arbitrary pair of states (A_1, A_2) of an arbitrary system A, and consider the energy changes $(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}$ and $(\Delta E_{R^o})^{\mathrm{sW,rev}}_{A_1A_2}$, respectively, in standard reversible weight processes $(A_1R_1 \rightarrow A_2R_2)^{\mathrm{rev}}_{\mathrm{sW}}$ and $(A_1R^o_1 \rightarrow A_2R^o_2)^{\mathrm{rev}}_{\mathrm{sW}}$. We call *temperature* of R the positive quantity

$$T_R = T_{R^o}\,\frac{(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}}{(\Delta E_{R^o})^{\mathrm{sW,rev}}_{A_1A_2}}\ , \tag{3}$$

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

Corollary 1. The ratio of the temperatures of two thermal reservoirs

$$\frac{T_{R'}}{T_{R''}} = \frac{(\Delta E_{R''})^{\mathrm{sW,rev}}_{A_1A_2}}{(\Delta E_{R''})^{\mathrm{sW,rev}}_{A_1A_2}} \tag{4}$$

is independent of the choice of the reference thermal reservoir and can be measured directly.

Corollary 2. Let (A_1, A_2) be any pair of states of a system A and let $(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}$ be the energy change of a thermal reservoir R, with temperature T_R, in any reversible standard weight process $(A_1R_1 \to A_2R_2)^{\mathrm{rev}}_{\mathrm{sW}}$. Then, for the given system A the ratio $(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}/T_R$ depends only on the pair of states (A_1, A_2), i.e., this ratio is independent of the choice of reservoir R and of its initial stable equilibrium state R_1.

Definition of property entropy. Let $(A_1\ , A_2)$ be any pair of states of a system A and let R be an arbitrarily chosen thermal reservoir. We call *entropy difference* between A_2 and A_1 the quantity

$$S(A_2) - S(A_1) = -\frac{(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}}{T_R}\ , \tag{5}$$

where $(\Delta E_R)^{\mathrm{sW,rev}}_{A_1A_2}$ is the energy change of R in any reversible standard weight process $(A_1R_1 \to A_2R_2)^{\mathrm{rev}}_{\mathrm{sW}}$ and T_R is the temperature of R. On account of Corollary 2, the right hand side of Eq. 5 is determined uniquely by states A_1 and A_2; therefore, entropy is a property of A.

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

$$S(A_1) - S(A_0) = -\frac{(\Delta E_R)^{\mathrm{sW,rev}}_{A_0A_1}}{T_R}\ . \tag{6}$$

Such a process exists for every state A_1, on account of assumption 3.

Theorem 4. If $C_1 = A_1B_1$ and $C_2 = A_2B_2$ are arbitrarily chosen states of a composite system $C = AB$, then

$$S(C_2) - S(C_1) = S(A_2) - S(A_1) + S(B_2) - S(B_1)\ . \tag{7}$$

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

Theorem 5. Let (A_1, A_2) be any pair of states of a system A and let R be a thermal reservoir with temperature T_R. Let $(A_1R_1 \to A_2R_2)^{\mathrm{irr}}_{\mathrm{W}}$ be any irreversible standard weight process and let $(\Delta E_R)^{\mathrm{sW,irr}}_{A_1A_2}$ be the energy change of R in this process. Then

$$-\frac{(\Delta E_R)^{\mathrm{sW,irr}}_{A_1A_2}}{T_R} < S(A_2) - S(A_1)\ . \tag{8}$$

Theorem 6. Let $(A_1 \to A_2)_W$ be any weight process for a system A. Then, the entropy difference $S(A_2) - S(A_1)$ is equal to zero if and only if the process is reversible; it is strctly positive if and only if the process is irreversible.

CONCLUSIONS

In this paper we provide a most concise but rigorous definition of entropy based on operative definitions of all the concepts employed in the treatment. The concept of heat is not employed and all assumptions are stated explicitly.

The domain of validity of the definition coincides with that of Assumption 3: every pair of states (A_1, A_2) of a system A can be interconnected by a reversible standard weight process for AR, where R is an arbitrarily chosen thermal reservoir. Since also the concept of quasi-static process is not used, the domain of validity of this definition of entropy is very general, and is not necessarily restricted to stable-equilibrium states or to local stable-equilibrium states of A. Moreover, since also the concepts of 'macroscopicity' and 'mesoscopicity' of the system are not used, and since no assumptions need to be made about the size of the region of space occupied by the system and the number of material particles in it, the definition holds as well for microscopic systems.

Therefore, as already emphasized in Ref. [1], where a less concise but equivalent definition was first presented, our carefully devised logical sequence yields a rigorous and sound generalization of the Clausius definition of entropy that extends from the usual thermodynamic equilibrium domain, to the domains of non-equilibrium states and of microscopic systems, which are of extreme importance to applications. Perhaps quite surprisingly, such important gains in generality are accompanied by a gain also in the simplicity of the exposition. Indeed, in our graduate and undergraduate teaching experience this approach has proved to be much superior than the obsolete traditional heuristic definitions cited in footnote 1, not only for its sound logical consistency, but also for the unifying basis it provides towards the understanding of non-equilibrium and microscopic phenomena.

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