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Highest-entropy, lowest-energy and lowest-volume principles

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Abstract — A statement of the lowest-volume principle, which holds both for simple systems and for collections of simple systems, is proved. Moreover, new proofs of the highest-entropy and of the lowest-energy principles, for simple systems and for collections of simple systems, are presented. The extremum principles proved in this paper hold for every set of states in which entropy is defined.

thermodynamics / criteria for stable equilibrium / lowest volume

Nomenclature

A	simple system	
a	constant	K
C	collection of simple systems, each in stable equilibrium	
c_v	molar specific heat at constant volume	J·mol^{-1}·K^{-1}
f	force	N
M	elementary mechanical system	
N	number of moles	mol
N_i	number of moles of the ith constituent	mol
$N_i^{(k)}$	number of moles of the ith constituent, in the kth region of space	mol
N	composition vector	mol
$\mathbf{N}^k$	composition vector in the kth region of space	mol
$p^{(m)}$	pressure of $\mathsf{Y}^{(m)}$	Pa
Q	quantity of heat	J
q	heat flux density	W·m^{-2}
q_i	ith component of **q**	W·m^{-2}
R	heat reservoir	
R	universal gas constant	J·mol^{-1}·K^{-1}
r	position	m
S	entropy	J·K^{-1}
s	entropy per unit mass	J·kg^{-1}·K^{-1}
T	thermodynamic temperature	K
T_R	thermodynamic temperature of R	K
$T^{(i)}$	thermodynamic temperature of $\mathsf{Y}^{(i)}$	K
U	energy, internal energy	J
u	energy per unit mass	J·kg^{-1}
V	volume	m^3
$V^{(i)}$	volume of the ith region of space, of $\mathsf{Y}^{(i)}$	m^3
v	volume per unit mass	m^3·kg^{-1}
W	quantity of work	J
X	system which performs a cycle	
Y	collection of simple systems	
$Y^{(i)}$	ith subsystem of Y	

Greek symbols

δ_{ij}	Kronecker delta	
λ_{ij}	tensor	m^7·kg^{-1}·W^{-2}
λ	scalar such that $\lambda_{ij} = \lambda\delta_{ij}$	m^7·kg^{-1}·W^{-2}
Ω	set of states of Y	
$\widetilde{\Omega}$	subset of Ω	

Subscripts

g	state of any kind
n	nonequilibrium state
s	stable equilibrium state
2s, 3s, 4s	stable equilibrium states
0	reference value of a property
1	initial state, initial value of a property

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1. INTRODUCTION

Two different forms of both the highest-entropy principle and the lowest-energy principle have been presented in treatments of thermodynamics. One of these forms has been proposed by Callen [1], the other by Gyftopoulos and Beretta [2]. Callen's extremum principles refer to a collection C of simple systems, such that the subsystems are separated by internal constraints and each of them passes through stable equilibrium states only. The highest-entropy principle, for instance, characterizes a stable equilibrium state of C as the highest-entropy one in the manifold of states of C which have fixed internal constraints and fixed values of the energy and of the volume. This form of the highest-entropy and of the lowest-energy principles can be used to establish the conditions for the mutual stable equilibrium of systems which are separately in equilibrium. On the other hand, Gyftopoulos–Beretta's extremum principles hold for every system and for every set of states in which entropy is defined. For instance, the highest-entropy principle stated by Gyftopoulos and Beretta is as follows: among the many states of a system that have given values of the energy, of the amounts of constituents and of the parameters, the entropy of the unique stable equilibrium state is larger than that of any other state with the same values of energy, amounts of constituents and parameters. This statement does not require the existence of either internal constraints or subsystems which pass through stable equilibrium states only.

In recent years, extended theories of irreversible thermodynamics, which analyze local nonequilibrium states, have been presented. In these theories, as well as in [2], it is assumed that entropy is defined even for local nonequilibrium states. Among these theories, let us recall, for instance, that presented in [3]. In order to check if an extended theory of irreversible thermodynamics is compatible with the basic laws of thermodynamics, extremum principles which hold for local nonequilibrium states can be useful. For instance, it is easily shown that the theory of extended irreversible thermodynamics presented in [3] is in agreement with Gyftopoulos–Beretta's statement of the highest-entropy principle. The consistency of other extended theories of irreversible thermodynamics with the highest-entropy principle is analyzed in [4].

Some years ago, Kazes and Cutler [5] have shown, through a mathematical argument, that for a pair of simple systems separated by an internal constraint Callen's highest-entropy principle may imply a lowest-volume principle, if the pressure of each simple system is positive. In a more recent study, Dunning-Davies [6] has stated that, for a simple system without internal constraints and with a fixed number of particles, no lowest-volume principle seems deducible. No statement of the lowest-volume principle endowed with a broader validity than that obtained in [5] is available in the literature.

In the present paper, statements of the highest-entropy, of the lowest-energy and of the lowest-volume principles which hold for any collection of simple systems, both in the presence and in the absence of internal constraints, for every set of states in which entropy is defined, are proved from the formulation of the second law of thermodynamics recently presented by Barletta and Zanchini [7]. Moreover, with reference to simple systems, it is shown that the lowest-energy and the lowest-volume principles can be deduced from the highest-entropy principle. Then, the lowest-volume principle is illustrated by an example. Finally, an application of the lowest-volume principle to extended theories of irreversible thermodynamics is presented.

The statements of the highest-entropy and of the lowest-energy principles presented here are similar to those proposed by Gyftopoulos and Beretta [2]. However, the proofs presented in this paper, for simple systems and collections of simple systems, do not require the assumption that any spontaneous process from a lower-entropy state to a higher-entropy state can take place.

2. HIGHEST-ENTROPY, LOWEST-ENERGY AND LOWEST-VOLUME PRINCIPLES

Let us recall Callen's treatment of the highest-entropy principle [1]. First, *simple systems* are defined as "*systems that are macroscopically homogeneous, isotropic, and uncharged, that are large enough so that surface effects can be neglected, and that are not acted by electric, magnetic, or gravitational fields*". Then, the following postulates are stated.

> "**Postulate I**. There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the mole numbers $N_1, N_2, \ldots, N_r$ of the chemical components."

> "**Postulate II**. There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states."

Postulate II is Callen's highest-entropy postulate. Clearly, it refers only to composite systems, with internal constraints, such that the constituent subsystems are in equilibrium. Postulate I is not completely satisfactory, because the author does not state a definition of equilibrium state. We will show that, if postulate I is replaced by a proper definition of *stable equilibrium state* and by the statement of the second law presented by Barletta and Zanchini [7], then a statement of the highest-entropy principle simpler and more general than postulate II can be *proved*.

In this paper, in analogy with the treatment presented by Callen [1], we will refer either to simple systems or to collections of simple systems, separated by internal walls or semi-permeable walls. We will describe the matter of each system by means of the mole numbers of its nonreactive constituents, i.e., of constituents whose mole numbers cannot change if the system is closed. Let us define an *equilibrium state* as a state which can be reproduced as a time-invariant state of an isolated system [8], and a *stable equilibrium state* as an equilibrium state which cannot be modified by a process that leaves no net changes of the positions of the walls and of the semi-permeable walls of the system and that leaves no net effects in the environment [8]. Moreover, let us call *elementary mechanical system* an auxiliary system M such that: the matter of M gives negligible contributions to gravitational, electric and magnetic fields; every state of M is uniquely determined by the position $\mathbf{r}$ of a material point of M, to which an external force $\mathbf{f}$ determined by $\mathbf{r}$ is applied [9]. An example of elementary mechanical system is a system which undergoes an infinitely slow translation in a uniform gravitational field, without any other change of state, under the effect of a constant external force [9]. Let us state the second law of thermodynamics as follows [7].

- Let Y be a collection of simple systems, and let $V^{(1)}, V^{(2)}, \ldots, V^{(m)}$ be the volumes of the regions of space bounded by walls which constrain the matter of Y. Let $\mathbf{N}^{(k)}$ be a vector whose components represent the mole numbers of the nonreactive constituents of Y constrained in the region with volume $V^{(k)}$. For every choice of $V^{(1)}, V^{(2)}, \ldots, V^{(m)}, \mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$, and of the energy U of Y there exists a unique stable equilibrium state of Y.

If no internal semi-permeable wall is present, the interpretation of this statement of the second law is very simple. In the presence of internal semi-permeable walls, the correct interpretation will be illustrated by an example. Let us suppose that system Y has two nonreactive constituents and is divided in two parts by an internal wall impermeable to the first constituent and permeable to the second. Let us call $V^{(1)}$ the volume of one subsystem, $N_1^{(1)}$ the number of moles of the first constituent contained in this subsystem, $V^{(2)}$ the total volume, $N_1^{(2)}$ and $N_2^{(2)}$ the mole numbers of the first and of the second constituent contained in the total volume. Then, for every set of values of $V^{(1)}, V^{(2)}, N_1^{(1)}, N_1^{(2)}, N_2^{(2)}$ and of the energy U of Y there exists a unique stable equilibrium state of Y.

For the special case of a simple system, which has no internal wall or semi-permeable wall and thus a unique volume V and a unique composition vector $\mathbf{N} = (N_1, N_2, \ldots, N_r)$, the second law stated above can be written as follows.

- If A is any simple system, then for every set of values of the energy U of A, of the volume V of A and of the mole numbers $N_1, N_2, \ldots, N_r$ of the constituents of A there exists a unique stable equilibrium state of A.

Note that, in this particular case, the statement of the second law becomes very similar to Callen's postulate I.

Let us now prove that the statement of the second law reported above implies a highest-entropy principle, a lowest-energy principle and a lowest-volume principle for every collection of simple systems.

THEOREM 1. HIGHEST-ENTROPY PRINCIPLE. – *Let Y be any collection of simple systems. Among all the states of Y which have given volumes $V^{(1)}, V^{(2)}, \ldots, V^{(m)}$ of the regions of space in which the matter of Y is constrained, given composition vectors $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ of the matter constrained in these regions of space and a given value of the energy U of Y, the unique stable equilibrium state is the highest-entropy state.*

Proof. – Given $V^{(1)}, V^{(2)}, \ldots, V^{(m)}$, $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ and U, let Y_s be the corresponding stable equilibrium state of Y and Y_g be any other state of Y. We will prove that $S(\mathsf{Y}_\mathrm{g}) < S(\mathsf{Y}_\mathrm{s})$. Let us assume that $S(\mathsf{Y}_\mathrm{g}) \geq S(\mathsf{Y}_\mathrm{s})$. Let us consider a reversible process $\mathsf{Y}_\mathrm{s} \to \mathsf{Y}_\mathrm{g}$ of an isolated system Y + R + X + M, where R is a heat reservoir with temperature T_R, X is any system which performs a cycle and M is an elementary mechanical system. This process exists. In fact, since the entropy difference $S(\mathsf{Y}_\mathrm{g}) - S(\mathsf{Y}_\mathrm{s})$ is defined, there exists a reversible process $\mathsf{Y}_\mathrm{s} \to \mathsf{Y}_\mathrm{g}$ of a proper isolated system such that system Y performs work on M and receives an infinite number of infinitesimal heat quantities δQ, each from a heat reservoir at a temperature T [10]. All heat reservoirs except one, which will be denoted by R, can be restored to their initial states by means of a reversible cyclic apparatus, X. When this has been done, a reversible process $\mathsf{Y}_\mathrm{s} \to \mathsf{Y}_\mathrm{g}$ of an isolated system Y + R + X + M has been obtained.

If one denotes by Q the quantity of heat which has been taken from R, the entropy change of R in this process is $-Q/T_\mathsf{R}$. On the other hand, since the process is reversible and $\mathsf{Y}+\mathsf{R}+\mathsf{X}+\mathsf{M}$ is isolated, the entropy change of $\mathsf{Y}+\mathsf{R}$ is zero. Therefore one has, in the process under exam,

$$S(\mathsf{Y}_\mathrm{g}) - S(\mathsf{Y}_\mathrm{s}) = \frac{Q}{T_\mathsf{R}} \tag{2.1}$$

The assumption $S(\mathsf{Y}_\mathrm{g}) \geq S(\mathsf{Y}_\mathrm{s})$ and equation (2.1) yield $Q \geq 0$. However, this result is impossible. In fact, since the energy of Y is unchanged, if $Q = 0$ the stable equilibrium state Y_s of Y has been modified without net changes of the positions of the walls and of the semi-permeable walls of Y and without net effects in the environment of Y, contrary to the definition of stable equilibrium state. If $Q > 0$, then a positive work $W = Q$ has been performed. As is well known, this work can be dissipated into R. After this has been done, when R has reached again its initial stable equilibrium state, the same condition discussed above for $Q = 0$ has been obtained. □

THEOREM 2. LOWEST-ENERGY PRINCIPLE. – *Let* Y *be any collection of simple systems. Among all the states of* Y *which have given volumes* $V^{(1)}, V^{(2)}, \ldots, V^{(m)}$ *of the regions of space in which the matter of* Y *is constrained, given composition vectors* $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ *of the matter constrained in these regions of space and a given value of the entropy* S *of* Y*, the unique stable equilibrium state is the lowest-energy state.*

Proof. – Given $V^{(1)}, V^{(2)}, \ldots, V^{(m)}$, $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ and S, let Y_s be the corresponding stable equilibrium state of Y and Y_s be any other state of Y. We will prove that $U(\mathsf{Y}_\mathrm{g}) > U(\mathsf{Y}_\mathrm{s})$. Let us assume that $U(\mathsf{Y}_\mathrm{g}) \leq U(\mathsf{Y}_\mathrm{s})$. Let us consider a reversible process $\mathsf{Y}_\mathrm{s} \rightarrow \mathsf{Y}_\mathrm{g}$ of an isolated system $\mathsf{Y}+\mathsf{R}+\mathsf{X}+\mathsf{M}$, where R is a heat reservoir with temperature T_R, X is any system which performs a cycle and M is an elementary mechanical system. Since the entropy difference $S(\mathsf{Y}_\mathrm{g}) - S(\mathsf{Y}_\mathrm{s})$ is defined, this process exists, as it has been proved in theorem 1. In this process, the entropy of Y remains unchanged on account of the assumption $S(\mathsf{Y}_\mathrm{g}) = S(\mathsf{Y}_\mathrm{s})$ and the entropy of $\mathsf{Y}+\mathsf{R}$ remains unchanged because the process of the isolated system $\mathsf{Y}+\mathsf{R}+\mathsf{X}+\mathsf{M}$ is reversible. Therefore the entropy of R remains unchanged, so that the quantity of heat Q taken from R is zero. If $U(\mathsf{Y}_\mathrm{g}) = U(\mathsf{Y}_\mathrm{s})$, then the stable equilibrium state Y_s of Y has been modified without net changes of the positions of the walls and of the semi-permeable walls of Y and without net effects in the environment of Y, contrary to the definition of stable equilibrium state. If $U(\mathsf{Y}_\mathrm{g}) < U(\mathsf{Y}_\mathrm{s})$, then a positive work W has been performed. By dissipating this work into Y, for instance by a stirrer, it is possible to bring Y in a nonequilibrium state Y_n, without net changes of the positions of the walls and of the semi-permeable walls of Y. Thus, the stable equilibrium state Y_s of Y has been modified without net changes of the positions of the walls and of the semi-permeable walls of Y and without net effects in the environment of Y, contrary to the definition of stable equilibrium state. □

Before presenting the statement and the proof of the lowest-volume principle for any collection of simple systems, we must prove the following lemma.

LEMMA 1. – *Let* Y *be any collection of simple systems. For every choice of the energy* U *of* Y*, of the entropy* S *of* Y*, of the composition vectors* $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ *in the regions of space in which the matter of* Y *is constrained, of the volumes* $V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}$ *of these regions of space, except one, there exists a unique stable equilibrium state of* Y.

Proof. – Let Ω be the set of the stable equilibrium states of Y which have the same values of U, $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$, $V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}$. On account of the second law of thermodynamics, for every value of $V^{(m)}$ there exists a unique stable equilibrium state of Y in Ω. Since $U, \mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}, V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}$ are fixed, the Gibbs relation for Y in Ω yields [11, 12]

$$\mathrm{d}U = T\,\mathrm{d}S - p^{(m)}\,\mathrm{d}V^{(m)} = 0 \tag{2.2}$$

where $p^{(m)}$ is the pressure of the mth subsystem of Y and T is the thermodynamic temperature of Y. From equation (2.2) one obtains

$$\mathrm{d}S = \frac{p^{(m)}}{T}\,\mathrm{d}V^{(m)} \tag{2.3}$$

Since both $p^{(m)}$ and T can assume only positive values, equation (2.3) shows that, in Ω, the entropy S of Y is a strictly increasing function of $V^{(m)}$. Therefore, a single valued function $V^{(m)}(S)$ exists in Ω. Moreover, for every prescribed value of S there exists in Ω a unique stable equilibrium state of Y, determined by the value of the function $V^{(m)}(S)$. □

THEOREM 3. LOWEST-VOLUME PRINCIPLE. – *Let* Y *be any collection of simple systems. Among all the states of* Y *which have given composition vectors* $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ *in the regions of space in which the matter of* Y *is constrained, given volumes* $V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}$ *of these regions of space, except one, given values of the energy* U *and of the entropy* S *of* Y*, the unique stable equilibrium state is the lowest-volume state.*

Proof. – Let Y_s be the stable equilibrium state of Y with volumes $V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}, V_s^{(m)}$, composition vectors $\mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}$ in these regions of space, total energy U and total entropy S. Let us assume that there exists another state Y_g of Y with the same values of $V^{(1)}, V^{(2)}, \ldots, V^{(m-1)}, \mathbf{N}^{(1)}, \mathbf{N}^{(2)}, \ldots, \mathbf{N}^{(m)}, U$ and S, and such that $V_g^{(m)} \leq V_s^{(m)}$. This assumption is not legitimate for the following reasons. Let us consider a reversible process $\mathsf{Y}_s \to \mathsf{Y}_g$ of an isolated system $\mathsf{Y} + \mathsf{R} + \mathsf{X} + \mathsf{M}$, where R is a heat reservoir with temperature T_R, X is any system which performs a cycle and M is an elementary mechanical system. As it has been proved in theorem 1, this process exists because the entropy difference $S(\mathsf{Y}_g) - S(\mathsf{Y}_s)$ is defined. Moreover, since both the energy and the entropy of Y are unchanged, it is easily verified that no net effect in the environment of Y exists in this process. If $V_g^{(m)} = V_s^{(m)}$, then the stable equilibrium state Y_s of Y has been modified without net changes of the positions of the walls and of the semi-permeable walls of Y and without net effects in the environment of Y, contrary to the definition of stable equilibrium state. If $V_g^{(m)} < V_s^{(m)}$, starting from state Y_g it is possible to restore the mth subsystem of Y to its original volume $V_s^{(m)}$, without net effects in the environment of Y, by means of a sudden displacement of the walls of this subsystem, in empty space. In this way, Y is brought to a nonequilibrium state, Y_n. Thus, through the combined process $\mathsf{Y}_s \to \mathsf{Y}_g \to \mathsf{Y}_n$, system Y has been brought from the stable equilibrium state Y_s to the nonequilibrium state Y_n without net changes of the positions of the walls and of the semi-permeable walls of Y and without net effects in the environment of Y, contrary to the definition of stable equilibrium state. □

Clearly, the statements and the proofs of theorems 1–3 and of lemma 1 hold, in particular, for simple systems. In this case, they can be written in a simpler form, but, conceptually, remain unchanged. In the following, we will write the statements of the extremum principles for simple systems. Then, with reference to simple systems, we will prove that both the lowest-energy principle and the lowest-volume principle can be deduced from the highest-entropy principle. It is easily verified that the deduction could be repeated for collections of simple systems.

HIGHEST-ENTROPY PRINCIPLE FOR SIMPLE SYSTEMS. – *Among all the states of a simple system* A *which have given values of the energy* U*, of the volume* V *and of the mole numbers* $N_1, N_2, \ldots, N_r$ *of the nonreactive constituents, the unique stable equilibrium state is the highest-entropy state.*

LOWEST-ENERGY PRINCIPLE FOR SIMPLE SYSTEMS. – *Among all the states of a simple system* A *which have given values of the entropy* S*, of the volume* V *and of the mole numbers* $N_1, N_2, \ldots, N_r$ *of the nonreactive constituents, the unique stable equilibrium state is the lowest-energy state.*

LOWEST-VOLUME PRINCIPLE FOR SIMPLE SYSTEMS. – *Among all the states of a simple system* A *which have given values of the energy* U*, of the entropy* S *and of the mole numbers* $N_1, N_2, \ldots, N_r$ *of the nonreactive constituents, the unique stable equilibrium state is the lowest-volume state.*

Proof. – Let A be any simple system, with fixed values of the mole numbers of its nonreactive constituents, and let A_1 be an arbitrarily chosen state of A, with energy U_1, volume V_1 and entropy S_1. Let us consider any process $\mathsf{A}_1 \to \mathsf{A}_{2s}$ of A, where A_{2s} is the stable equilibrium state of A with energy U_1 and volume V_1. On account of the highest-entropy principle, $S(\mathsf{A}_{2s}) > S_1$. In order to restore the entropy of A to its initial value S_1, without changing the volume V_1 of A, we can take heat from A, in a quasistatic and reversible process at constant volume $\mathsf{A}_{2s} \to \mathsf{A}_{3s}$ of A. Thus, in the stable equilibrium state A_{3s}, A has volume V_1, entropy S_1, and an energy $U(\mathsf{A}_{3s}) < U_1$. The lowest-energy principle has been proved, because $U(\mathsf{A}_{3s})$ is lower than the energy of an arbitrarily chosen state of A with volume V_1 and entropy S_1. Since the pressure of A is positive, we can restore the energy of A to its initial value U_1, without changing the entropy S_1 of A, by means of an adiabatic quasistatic and reversible compression $\mathsf{A}_{3s} \to \mathsf{A}_{4s}$ of A. In the final stable equilibrium state A_{4s}, A has energy U_1, entropy S_1, and a volume $V(\mathsf{A}_{4s}) < V_1$. Thus, the lowest-volume principle has been proved, because $V(\mathsf{A}_{4s})$ is lower than the volume of an arbitrarily chosen state of A with energy U_1 and entropy S_1. □

3. AN EXAMPLE ON THE LOWEST-VOLUME PRINCIPLE

The lowest-volume principle deduced in Section 2 will be illustrated by an example. Let $\mathsf{Y} = \mathsf{Y}^{(1)} + \mathsf{Y}^{(2)}$ be a composite system, such that $\mathsf{Y}^{(1)}$ and $\mathsf{Y}^{(2)}$ are identical simple systems, each composed of N moles of an ideal monoatomic gas. Let c_v be the molar specific heat at constant volume of this gas, which, as is well known, has the value $(3/2)R$, where R is the universal gas constant. On account of the lowest-volume principle, if Ω is the set of the states of Y with fixed values of U, S and $V^{(1)}$, the state of Ω in which the volume V of Y is minimum is the unique state of Ω which is a stable equilibrium state of Y. In this example, we will consider only the subset $\widetilde{\Omega}$ of Ω which is composed of stable equilibrium states of $\mathsf{Y}^{(1)}$ and of $\mathsf{Y}^{(2)}$. We will show that the state of $\widetilde{\Omega}$ in which the volume V of Y is minimum is the unique state of $\widetilde{\Omega}$ which is a stable equilibrium state of Y.

The internal energy of an ideal monoatomic gas in stable equilibrium, with N moles and temperature T, is given by

$$U - U_0 = Nc_v(T - T_0) \tag{3.1}$$

where T_0 is a reference temperature and U_0 is the internal energy value assigned to the system at temperature T_0. If one chooses $U_0 = 0$, equation (3.1) yields

$$U = Nc_v(T - T_0) \tag{3.2}$$

By applying equation (3.2) to $\mathsf{Y}^{(1)}$ and to $\mathsf{Y}^{(2)}$ and by employing the additivity of energy, one obtains the following expression of the energy of Y, for every state of Y which belongs to $\widetilde{\Omega}$:

$$U = Nc_v\big(T^{(1)} + T^{(2)} - 2T_0\big) \tag{3.3}$$

where $T^{(1)}$ is the temperature of $\mathsf{Y}^{(1)}$ and $T^{(2)}$ is the temperature of $\mathsf{Y}^{(2)}$.

The entropy of an ideal monoatomic gas in stable equilibrium, with N moles, temperature T and volume V, is given by

$$S - S_0 = Nc_v \ln\frac{T}{T_0} + NR\ln\frac{V}{V_0} \tag{3.4}$$

where V_0 is a reference volume and S_0 is the entropy value assigned to the system at temperature T_0 and volume V_0. If one chooses $S_0 = 0$, equation (3.4) yields

$$S = Nc_v \ln\frac{T}{T_0} + NR\ln\frac{V}{V_0} \tag{3.5}$$

By applying equation (3.5) to $\mathsf{Y}^{(1)}$ and to $\mathsf{Y}^{(2)}$ and by employing the additivity of entropy, one obtains the following expression of the entropy of Y, for every state of Y which belongs to $\widetilde{\Omega}$:

$$S = Nc_v \ln\frac{T^{(1)}T^{(2)}}{T_0^2} + NR\ln\frac{V^{(1)}V^{(2)}}{V_0^2} \tag{3.6}$$

It is easily verified that there exist infinite values of $V^{(2)}$ which fulfil equations (3.3) and (3.6) with prescribed values of U, S and $V^{(1)}$; therefore, the set $\widetilde{\Omega}$ contains infinite states. We will now prove that, among these states, one and only one minimizes $V^{(2)}$, and thus V, and is a stable equilibrium state of Y.

From equation (3.6), one obtains

$$\ln\frac{V^{(1)}V^{(2)}}{V_0^2} = \frac{1}{NR}\left(S - Nc_v\ln\frac{T^{(1)}T^{(2)}}{T_0^2}\right) \tag{3.7}$$

Since the natural logarithm is a strictly increasing function, on account of equation (3.7) the product $V^{(1)}V^{(2)}$ is minimum if and only if the product $T^{(1)}T^{(2)}$ is maximum. Obviously, the minimum value of $V^{(1)}V^{(2)}$ corresponds to the minimum value of $V^{(2)}$ and of V, because the value of $V^{(1)}$ is prescribed. The product $T^{(1)}T^{(2)}$ is maximum if and only if $T^{(1)} = T^{(2)} = T$. In fact, if we consider another state of $\widetilde{\Omega}$ such that the temperature of $\mathsf{Y}^{(1)}$ is $T + a$, then the temperature of $\mathsf{Y}^{(2)}$ in this state is necessarily $T - a$, in order to keep the total energy of Y unchanged. For every nonvanishing value of a, the following inequality holds:

$$(T + a)(T - a) = T^2 - a^2 < T^2 \tag{3.8}$$

Let us consider the state of $\widetilde{\Omega}$ such that $T^{(1)} = T^{(2)} = T$. This state exists and is unique. In fact, with this additional constraint, equation (3.3) allows one to determine the temperature T; then equation (3.6) allows one to determine a unique value of $V^{(2)}$. Moreover, this state is the unique stable equilibrium state of Y in $\widetilde{\Omega}$, because only this state fulfils the necessary condition for the mutual stable equilibrium of $\mathsf{Y}^{(1)}$ and $\mathsf{Y}^{(2)}$, namely $T^{(1)} = T^{(2)} = T$. Therefore, the unique stable equilibrium state of Y which belongs to $\widetilde{\Omega}$ is the unique state of $\widetilde{\Omega}$ which minimizes the volume V of Y.

4. THE LOWEST-VOLUME PRINCIPLE AND GENERALIZED THEORIES OF IRREVERSIBLE THERMODYNAMICS

In generalized theories of irreversible thermodynamics, where local nonequilibrium states are considered, it is assumed that the generalized entropy per unit mass s of a medium depends not only on the energy u and on the volume v per unit mass, but also on other variables. For instance, in extended irreversible thermodynamics [3], it is assumed that the generalized entropy per unit mass of a fluid depends not only on u and v, but also on the components of the heat flux density $\mathbf{q}$ and of the stress tensor. This assumption implies that, for nonviscous fluids, s depends on u, v and $\mathbf{q}$. For these fluids, one could assume that the volume per unit mass v depends not only on the energy u and the entropy s per unit mass, but also on the heat flux density $\mathbf{q}$. More precisely, in analogy with the treatment presented in [3], one could guess that, for these fluids, the relation between v, u, s, and $\mathbf{q}$ is

$$v = v_0(u,s) + \lambda_{ij}(u,s) q_i q_j \tag{4.1}$$

where $v_0(u,s)$ is the specific volume in the stable equilibrium state with specific energy u and specific entropy s, while $\lambda_{ij}(u,s)$ is a symmetric tensor. The lowest-volume principle yields a constraint on $\lambda_{ij}(u,s)$, i.e. that $\lambda_{ij}(u,s)$ is positive definite. In particular, if $\lambda_{ij}(u,s)$ is isotropic, the scalar λ such that $\lambda_{ij}(u,s) = \lambda(u,s)\delta_{ij}$ must be positive. In this case, equation (4.1) can be rewritten as

$$v = v_0(u,s) + \lambda(u,s)\mathbf{q}\cdot\mathbf{q} \tag{4.2}$$

Equation (4.2) implies that, if heat transfer occurs in a nonviscous fluid, for fixed values of u and s the volume per unit mass is an increasing function of the modulus of $\mathbf{q}$.

Let us point out that the constraint on $\lambda_{ij}(u,s)$ stated above could not be obtained, in general, by employing either the highest-entropy principle or the lowest-energy principle.

5. CONCLUSIONS

The highest-entropy, the lowest-energy and the lowest-volume principles have been deduced from a recent formulation of the second law of thermodynamics. The statements proved here hold for any collection of simple systems, including one simple system, and for any set of states in which entropy is defined. On the contrary, Callen's statements of the highest-entropy and of the lowest-energy principles apply only to composite systems with internal constraints, such that each subsystem is in a stable equilibrium state. The lowest-volume principle proved in this paper yields restrictions on the possible values of the volume per unit mass, in the framework of generalized theories of irreversible thermodynamics.

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REFERENCES

[1] Callen H.B., Thermodynamics and an Introduction to Thermostatistics, 2nd ed., Wiley, New York, 1985, Chapters 1, 5.

[2] Gyftopoulos E.P., Beretta G.P., Thermodynamics: Foundations and Applications, Macmillan, New York, 1991, Chapters 7, 8.

[3] Jou D., Casas-Vázquez J., Lebon G., Extended Irreversible Thermodynamics, Springer-Verlag, Berlin, 1993.

[4] Barletta A., Zanchini E., Unsteady heat conduction by internal-energy waves in solids, Phys. Rev. B 55 (1997) 14208–14213.

[5] Kazes E., Cutler P.H., Implications of the entropy maximum principle, Amer. J. Phys. 56 (1988) 560–561.

[6] Dunning-Davies J., Comment on "Implications of the entropy maximum principle", by E. Kazes and P.H. Cutler [Am. J. Phys. 56, 560–561 (1988)], Amer. J. Phys. 61 (1993) 88–89.

[7] Barletta A., Zanchini E., Thermodynamic equilibrium in dielectric fluids, Nuovo Cimento D 16 (1994) 189–203.

[8] Zanchini E., Barletta A., Finite-mass heat reservoirs and the second law, Nuovo Cimento B 110 (1995) 1245–1258.

[9] Zanchini E., Thermodynamics: Energy of nonsimple systems and second postulate, Nuovo Cimento B 107 (1992) 123–139.

[10] Fermi E., Thermodynamics, Prentice-Hall, Englewood Cliffs, NJ, 1937, Chapter 4.

[11] Callen H.B., Thermodynamics and an Introduction to Thermostatistics, 2nd ed., Wiley, New York, 1985, Chapter 2.

[12] Gyftopoulos E.P., Beretta G.P., Thermodynamics: Foundations and Applications, Macmillan, New York, 1991, Chapter 16.