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The mathematical formulation of the local form of the second principle of thermodynamics

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ABSTRACT. — The aim of this paper is to demonstrate that the so-called Clausius-Planck inequality represents the correct local formulation of the second principle of thermodynamics for single-phase continuous materials. A precise meaning is attributed to the concepts of state, reversibility, equilibrium process, etc., and the notion of entropy is defined both for equilibrium and non-equilibrium processes. The analysis shows that the Clausius-Planck inequality must be valid in general for non-equilibrium/ non-homogeneous processes provided, of course, that a macroscopic description of the process is possible.

RÉSUMÉ. — Le but de cet article est de démontrer que l'inégalité de Clausius-Planck représente la formulation locale correcte du deuxième principe de la thermodynamique pour le cas classique de matériaux continus ayant une phase unique. On attribue un sens précis aux concepts d'état, de réversibilité, de processus d'équilibre, etc., et on définit la notion d'entropie pour les processus d'équilibre et pour les processus au dehors de l'équilibre. On démontre que l'inégalité de Clausius-Planck doit être valide, en général, pour processus au dehors d'équilibre et pour processus non homogènes, pourvu que, naturellement, il soit possible de décrire ces processus d'un point de vue macroscopique.

1. INTRODUCTION

Local forms of the second principle of thermodynamics are often introduced in continuum mechanics as mathematical generalizations of well

established formulæ of classical thermodynamics. Of course, when these generalizations are pursued in an abstract way they may lead to relations which do not respect the original content of the second principle: impossibility of perpetual motion of the second kind (cf. [4], § 106-136). Serious doubts in this sense have been recently raised (cf. [8]) for the so-called local form of the Clausius-Duhem inequality. The aim of the present article is to deduce for single-phase continuous materials an analytical local condition which is both necessary and sufficient to exclude the occurrence of perpetual motions of the second kind. Such a condition should be regarded as the correct local formulation of the second principle for the materials in question.

The procedure we shall follow will be that of repeating the classical reasoning in a way appropriate to the application at which we are aiming. In doing so we shall have to emphasize the meaning of the main concepts introduced in classical thermodynamics. This is done in Sections 2 and 3 where a precise definition of the words *state, process, cycle, equilibrium* and *reversibility* is given. Section 4 deals with the mathematical formulation of the second principle in the classical case of homogeneous processes. The aim is to point out the fact that this formulation is *fully* expressed by a postulate relevant to cyclic processes performed by systems at uniform (but, of course, time depending) temperature. In Section 5, the concept of *reversible entropy* will be introduced and the way in which the notion of entropy has to be defined in the case of non-equilibrium/non-homogeneous processes will be discussed. This should provide an answer to the often raised questions on whether entropy can be defined in non-equilibrium situations, on whether entropy is a quantity which can be measured in non-reversible situations and on whether entropy is a quantity which can be uniquely defined (to within a constant) for each material. As a main result Section 5 contains the proof that the so-called Clausius-Planck inequality is the correct local form of the second principle of thermodynamics. The analysis should make clear that this inequality is valid in general for non-equilibrium/non-homogeneous processes provided, of course, that these processes are not so tumultuous that a macroscopic description of the phenomenon becomes meaningless.

2. THE DEFINITIONS OF STATE, PROCESS AND CYCLE

We shall define a *material system* (or more simply a *system* or a *body*) as a portion of matter whose behaviour we want to describe by means of a

suitable theoretical model. By *state* of the system we shall denote a collection of values assumed by the set of variables which are supposed to be sufficient to define the kinematical-physical-chemical situation of the system. The problem of selecting and identifying the state variables of a system is a problem which must be considered whenever we have to apply the theory to a specific system. This problem, however, can be disregarded in the present general analysis. From the definition of state it follows that two kinematical-physical-chemical situations of a system are the same whenever all the state variables assume the same values in both the situations.

A *process* is an ordered and continuous succession of states. Time may be assumed as parameter of this succession. We cannot assume, however, that time itself is a state variable if we suppose—as we shall do—that a system can be in the same state at two different instants.

Let t_1 and t_2 denote two values of time t. We shall say that a process occurring between t_1 and t_2 is a *cyclic process* (or a *cycle*) if the state of the system at $t = t_1$ is the same as the state of the system at $t = t_2$. Time rates of state variables may, of course, be state variables themselves. In a purely mechanical theory, for instance, to define the state variables of a material point we have to specify not only the position of the point but also its velocity and its acceleration: two material points in the same position but with different velocities and accelerations are, clearly, in different states according to the above definition of state. Similarly, when a thermodynamical theory is considered, the time rates of the absolute temperature θ are in general state variables. To be convinced about this observe for instance that the situation of a body at uniform but time-increasing temperature is certainly different from the situation in which the temperature of the body is constant (thermal equilibrium) or time-decreasing or time-increasing at different rate; all the other state variables being kept constant.

The above definitions of state and, consequently, of cycle are particularly useful in extending in an unambiguous way the results of classical thermodynamics to the macroscopic thermodynamics of non-homogeneous processes. Classical thermodynamics deals with equilibrium processes. For this reason quantities representing time rates are automatically excluded from the set of the variables of a system. It is concerned, moreover, mainly with the case in which the state variables do not vary throughout the system. In such a situation it is possible to develop the theory without introducing state variables which represent time rates or which can assume different values in the various parts of the system (cf. for instance the classical case of a gas undergoing an equilibrium process; in this case the state is defined by three numbers representing respectively the volume, the pressure and the temperature of the system). While this restricted notion of state is perfectly adequate to the scope of the classical theory, it has to be properly widened if we want to deal with non-homogeneous and/or non-equilibrium processes.

3. REVERSIBLE AND QUASI-STATIC PROCESSES

In classical thermodynamics the notion of reversibility is usually intro-
duced through the following or an equivalent definition (cf. *e. g.* [4], § 112
and [6], p. 12):

A process is reversible if: (*a*) it can be performed by a system both accord-
ing to the direct succession of states defining the process *(direct process)*
and according to the inverse succession *(inverse process)*; (*b*) during the
inverse process not only the system but also the surroundings recover the
same states they assume during the direct process.

A system is said to be in a *state of equilibrium* when all its state variables
which represent time rates vanish. Accordingly, an ordered succession of
states of equilibrium is called an *equilibrium* (or *quasi-static*) *process*. It
must be emphasized that a system can never undergo in a finite time interval
a quasi-static process which is different from the trivial one which always
keeps the system at the same state. For a system to pass from one equilibrium
state to another equilibrium state some state variables must change. Hence,
the time rates of these variables must be different from zero and, therefore,
the passage from an equilibrium state to another one cannot be accomplished
by a quasi-static process.

From the previous definitions we can infer that a reversible process must
be a quasi-static one. Indeed, during the inverse process the state variables
representing time rates assume opposite values to those they assume during
the direct process. Thus, they must vanish in order that during the inverse
process the system may attain the same states it attains during the direct
process.

Since a quasi-static process is not, in general, a real process, it follows
that a system cannot undergo in practice a reversible process which is
different from a trivial one which keeps the system at the same state. That
a reversible process in a mere theoretical abstraction which does not corres-
pond to any realizable process was pointed out effectively by Duhem ([3],
§ 58). However, Duhem *(loc. cit.)* considered quasi-static processes as
reversible; while according to the definitions here adopted a quasi-static
process is not, in general, a reversible one. This is better shown by the follow-
ing example. A bar of conducting material is kept at non-uniform temperature
by putting its ends in contact with two heat reservoirs at different tempera-
tures. If the reservoirs are big enough a steady-state situation will be reached
in which the bar is in an equilibrium state since all its state variables repre-
senting time rates vanish. In this situation, however, the state variables
vary along the bar since θ so does. We can regard the process undergone
by the bar during a certain time interval in the steady-state situation as a
trivial quasi-static process in which the state of the system does not change.

In the same steady-state situation we can regard the process undergone by the system during a successive time interval as the inverse of the above process. The latter is, therefore, trivially invertible. It is not, however, reversible because at the end of the inverse process the surroundings are in a different situation from that at the beginning of the direct process owing to the transfer of a certain amount of heat from one reservoir to the other.

The above example shows that there are equilibrium states which cannot belong to any reversible process. In the considered case this was a consequence of the presence of a stationary temperature gradient. In general, a given equilibrium state cannot belong to a reversible process if we cannot prevent the surroundings from undergoing changes in their state by keeping the system at the equilibrium state. To denote a state of equilibrium which can belong to a reversible process we shall adopt the expression *state of reversible equilibrium*.

4. THE SECOND PRINCIPLE OF THERMODYNAMICS

The second principle of thermodynamics can be expressed by one of the following equivalent postulates:

(A) *In a system of bodies at different temperatures it is impossible to transfer heat from a colder to a hotter body by means of a process which leaves undiminished the internal energy of the system and does not requires the expense of mechanical work by the surroundings.*

(B) *(Impossibility of perpetual motions of the second kind). It is impossible by means of an inanimate material agency to derive useful mechanical work from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

Postulate (A) is due in essence to Clausius [1] while postulate (B) was expressed by Kelvin [2]. It is well known that these two postulates are equivalent. The proof is simple and can be found in many books on thermodynamics (see *e. g.* [6] and [7]).

Let Q denote the amount of heat absorbed by a body in the unit time and suppose that the body undergoes a cyclic process. Let θ denote the absolute temperature of the body and suppose that during the cycle the body is at uniform temperature. Of course θ may depend on time. A mathematical formulation of postulates (A) and (B) is the following:

(C) *For **every system** undergoing a cycle at **uniform** (but in general time-depending) temperature θ the relation*

$$\oint_{\text{rev}} \frac{Q}{\theta}\, dt = 0 \qquad (4.1)$$

holds for reversible cycles. Whereas, if a cycle is not reversible the relation

$$\oint_{irr} \frac{Q}{\theta} \, dt < 0 \qquad (4.2)$$

must hold. In no cycle can the value of the above integral be positive.

In the above formulæ the symbol $\oint$ means integral along the cycle, while the indices *rev* and *irr* emphasize that the cycle is reversible or irreversible, respectively ([1]).

The hypothesis of uniform temperature is not only an essential part of postulate (C) but is also useful to eliminate any ambiguity in the meaning of the quantity θ in the integrals (4.1) and (4.2). This hypothesis by no way means that postulate (C) does not introduce any restriction in systems at non-uniform temperature. Since (C) applies to every system at uniform temperature it must apply, in particular, to each infinitesimal (and thus at uniform temperature) element of a system at non-uniform temperature. However, the very fact that (C) refers to systems or parts of them at uniform temperature entails that in (4.1) and (4.2) the quantity θ must be regarded as a function of t only. Any possible dependence of θ on the variables describing the position of the points of the system to which (4.1) and (4.2) are applied is excluded by the fact that postulate (C) is a statement relevant to portions of matter at uniform temperature.

The classical proof that (C) is equivalent to (A) or (B) hinges on the famous theorem on efficiency of heat engines enunciated by Carnot and proved in a correct way by Clausius ([2]). We are following, however, the brillant exposition by Fast ([6], p. 24-36) which has the advantage of establishing (4.1) and (4.2) without introducing the notion of entropy.

In classical single-phase continua the quantity Q is considered to be composed of the contributions of the *heating flux vector h* and of the *specific heating supply s*. We shall assume that h is outward directed with respect to the surface of the body whenever it represents an amount of heat which flows into the body in the unit time, and that s is positive whenever it

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([1]) It may be worthwile to remark that in postulate (C) it is tacitly assumed that Q does not vanish identically during the cycle. If $Q \equiv 0$ during the cycle, then (4.1) is satisfied irrespectively on whether it is applied to a reversible or to an irreversible cycle. It follows that postulate (C) is a non-trivial statement only when applied to a system (or a part of it) which loses or absorbs heat during the process. This is natural since the second principle is concerned with transformation of heat into work and, therefore, does not impose any restriction to systems undergoing processes in which each element does not absorb or lose any amount of heat.

([2]) The proof given by Carathéodory is free from any reference to heat engines. Its starting point, however, is a postulate of the second law which can be shown to be completely equivalent to the above (A), (B) or (C) (see [7], chap. 8).

represents an amount of heat absorbed by the body in the unit time. We can, therefore, express Q as

$$Q = \iint_{\partial B} \underset{\sim}{h} \cdot n dA + \iiint_B \rho s dV, \tag{4.3}$$

where ∂B is the external surface of the system B, n is the outward oriented unit normal to the surface element dA of ∂B, ρ is the mass density and dV is a volume element of B. By applying the divergence theorem we get from (4.3)

$$Q = \iiint_B (\mathrm{div}\, \underset{\sim}{h} + \rho s) dV. \tag{4.4}$$

When a system of infinitesimal volume is considered, we can exploit (4.4) and express (4.1) and (4.2) in the form

$$\oint_{\mathrm{rev}} \frac{1}{\theta} (\mathrm{div}\, \underset{\sim}{h} + \rho s) dt = 0 \tag{4.5}$$

and

$$\oint_{\mathrm{irr}} \frac{1}{\theta} (\mathrm{div}\, \underset{\sim}{h} + \rho s) dt < 0, \tag{4.6}$$

respectively. These relations can be considered as the local equivalent of (4.1) and (4.2).

5. LOCAL FORM OF THE SECOND PRINCIPLE IN THE CASE OF INFINITESIMAL PROCESSES

Relations (4.5) and (4.6) are relevant to cyclic processes. In practical applications, however, it is often convenient to express the second principle in a form which is valid for every infinitesimal process ([3]). This can be achieved by introducing the notion of entropy. In the case of reversible processes this notion is suggested spontaneously by equation (4.1): since (4.1) must be valid for an arbitrary reversible cycle, a well-known chain of reasoning leads to the conclusion that there must be a quantity H—a continuous and single-valued function of the variables defining the states of reversible equilibrium—with the property that

$$dH = \frac{Q}{\theta} dt. \tag{5.1}$$

([3]) By an infinitesimal process we understand a process relevant to an infinitesimal variation of t; t being considered as parameter for the states assumed by the system during a process.

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The quantity H is usually called entropy; it is defined by (5.1) to within an arbitrary constant. We shall adopt for H the denomination of *reversible entropy* to emphasize that this function is defined by (5.1) for states of reversible equilibrium only. Once the quantity H is introduced, we can obtain from (4.1) the relations

$$\oint_{\text{rev}} \frac{Q}{\theta} dt = \int_{1}^{2} \frac{Q}{\theta} dt + \int_{2}^{1} \frac{Q}{\theta} dt = \int_{1}^{2} \frac{Q}{\theta} dt + \int_{2}^{1} dH = 0. \qquad (5.2)$$

Here 1 and 2 denote two states belonging to the reversible cycle taken into consideration. These states are, obviously, states of reversible equilibrium. Since the states 1 and 2 can be in the same infinitesimal neighbourhood, we deduce from $(5.2)_3$ that for reversible processes

$$Q = \theta \dot{H} \qquad (5.3)$$

which is the equivalent of (4.1) for the case of infinitesimal processes.

When considering a continuous material, it is convenient to introduce the quantity $\bar{\eta}$ defined by

$$H = \iiint_{B} \rho \bar{\eta} dV, \qquad (5.4)$$

We shall refer to $\bar{\eta}$ as to the *specific reversible entropy*. From (4.4) and (5.4) we can deduce the local form of (5.3):

$$\operatorname{div} \underset{\sim}{h} + \rho s = \rho \theta \dot{\bar{\eta}}. \qquad (5.5)$$

This relation holds for reversible processes because so does (5.3). Since for reversible processes grad $\theta \equiv 0$ (cf. end of Section 3), the term div $\underset{\sim}{h}$ should be dropped from (5.5) whenever the constitutive equation for $\underset{\sim}{h}$ is such that $h = 0$ if grad $\theta \equiv 0$. In particular, as Pipkin and Rivlin [5] proved that for central symmetric materials the vector $\underset{\sim}{h}$ must vanish if the temperature gradient vanishes, the term containing div $\underset{\sim}{h}$ should be dropped from (5.5) when central symmetric materials are considered.

Let us now focus our attention on the case of irreversible processes. Consider an irreversible process which takes the system from state 1 to state 2 and suppose that both 1 and 2 are states of reversible equilibrium. Once state 2 is reached, let the system be brought back to state 1 through a reversible process (this process is possible since states 1 and 2 are assumed to be states of reversible equilibrium). In this way we have constructed a cycle which is irreversible because the process from 1 to 2 is irreversible. From (4.2) and $(5.2)_3$ we get, therefore,

$$\oint_{\text{irr}} \frac{Q}{\theta} dt = \int_{1}^{2} \frac{Q}{\theta} dt + \int_{2}^{1} \frac{Q}{\theta} dt = \int_{1}^{2} \frac{Q}{\theta} dt + \int_{2}^{1} dH < 0. \qquad (5.6)$$

That is

$$\int_{\substack{1 \\ irr}}^{2} \frac{Q}{\theta} \, dt < \int_{1}^{2} d\mathrm{H}. \tag{5.7}$$

At this point the procedure usually followed in classical thermodynamics makes appeal to the fact that (5.7) must be valid in particular when states 1 and 2 are in the same infinitesimal neighbourhood and the process from 1 to 2 is an infinitesimal one. In this way it is inferred from (5.7) for irreversible processes

$$Q < \theta \dot{\mathrm{H}}. \tag{5.8}$$

Such a procedure does not seem correct. Since by hypothesis the states 1 and 2 which appear in (5.7) are states of reversible equilibrium and since an infinitesimal process between two states of reversible equilibrium in the same infinitesimal neighbourhood is a reversible one, it follows that for this process relation (5.3) must be valid and that, therefore, the above limit procedure cannot lead anywhere but to the same result (5.3).

To arrive at a relation analogous to (5.5) but valid also for irreversible processes consider two generic states (not necessarily of reversible equilibrium), say 1* and 2*, in addition to two states of reversible equilibrium, say 1 and 2. Suppose that the system undergoes a cyclic process composed of the following successive phases: a process from 1* to 2*, a process from 2* to 2, a reversible process from 2 to 1 and, finally, a process from 1 to 1* that completes the cycle. The processes (1*, 2*), (2*, 2) and (1, 1*) are, in general, non-reversible. In general, therefore, the cycle is irreversible and from (4.1) and (4.2) we can deduce that

$$\int_{1*}^{2*} \frac{Q}{\theta} \, dt + \int_{2*}^{2} \frac{Q}{\theta} \, dt + \int_{\substack{2 \\ rev}}^{1} \frac{Q}{\theta} \, dt + \int_{1}^{1*} \frac{Q}{\theta} \, dt \leq 0, \tag{5.9}$$

the equality sign holding when the cycle is reversible. By applying (5.9) to an infinitesimal element and recalling $(5.2)_3$, (5.4) and (4.4) we infer that

$$\int_{1*}^{2*} \frac{1}{\theta} (\mathrm{div} \, \underset{\sim}{h} + \rho s) dt \leq \int_{1}^{2} \rho \dot{\eta} dt - \int_{2*}^{2} \frac{Q}{\theta} \, dt - \int_{1}^{1*} \frac{Q}{\theta} \, dt \tag{5.10}$$

where in the last two integrals we have for simplicity kept the notation Q for div $\underset{\sim}{h} + \rho s$.

By introducing the quantity $\mathscr{H}_{(1,2,1*,2*)}$ defined by

$$\mathscr{H}_{(1,2,1*,2*)} = \int_{1*}^{1} \frac{Q}{\theta} \, dt + \int_{1}^{2} \rho \dot{\eta} dt + \int_{2}^{2*} \frac{Q}{\theta} \, dt, \tag{5.11}$$

we can write (5.10) in the form

$$\int_{1*}^{2*} \frac{1}{\theta} (\mathrm{div} \, \underset{\sim}{h} + \rho s) dt \leq \mathscr{H}_{(1,2,1*,2*)}. \tag{5.12}$$

Let $\mathscr{I}$ denote the space of the states of reversible equilibrium and let $\Pi(1^*, 2^*)$ be the set of all the couples of processes $(1, 1^*)$ and $(2^*, 2)$ for assigned 1^* and 2^*. As the couple of states $\{1, 2\}$ varies in $\mathscr{I}$ and as the couple of processes $\{(1, 1^*), (2^*, 2)\}$ varies in $\Pi(1^*, 2^*)$, the quantity $\mathscr{H}_{(1,3,1^*,2^*)}$ assumes different values. Let $\mathscr{H}_{(1^*,2^*)}$ denote the supremum of the values assumed by $\mathscr{H}_{(1,2,1^*,2^*)}$ for $\{1, 2\}\,\varepsilon\mathscr{I}$ and for $\{(1, 1^*), (2^*, 2)\}\,\varepsilon\Pi(1^*, 2^*)$, that is

$$\mathscr{H}_{(1^*,2^*)} = \sup_{\mathscr{I},\Pi(1^*,2^*)} \mathscr{H}_{(1,2,1^*,2^*)}. \qquad (5.13)$$

$\mathscr{H}_{(1^*,2^*)}$ is thus defined as a single-valued function of the states 1^* and 2^* and can assume any real value between $-\infty$ and $+\infty$. For simplicity we shall assume that $\mathscr{H}_{(1^*,2^*)}$ is a smooth function of the state variables defining 1^* and 2^*. Since relation (5.12) must be met for every choice of states 1 and 2 and for every process $(1, 1^*)$ and $(2^*, 2)$, it follows that

$$\int_{1^*}^{2^*} \frac{1}{\theta}(\mathrm{div}\ \underset{\sim}{h} + \rho s)dt \le \mathscr{H}_{(1^*,2^*)}. \qquad (5.14)$$

In particular when the process is an infinitesimal one (see footnote 3) which takes the system from the state 1^* to the state $\bar{1}^*$ in the infinitesimal neighbourhood of 1^*, we have from (5.14) that

$$\mathrm{div}\ \underset{\sim}{h} + \rho s \le \rho\theta\dot{\eta} \qquad (5.15)$$

where the quantity $\dot{\eta}$ is defined by the relation

$$\rho\dot{\eta}dt = \dot{\mathscr{H}}_{(1^*,\bar{1}^*)}. \qquad (5.16)$$

We shall call η the *specific entropy* of the material. Relation (5.15) is sometimes called Clausius-Planck inequality, it has been deduced here as a necessary consequence of postulate (C).

Since 1^* and $\bar{1}^*$ are not, in general, states of equilibrium, the entropy above defined is relevant to non-equilibrium states. From (5.11) and (5.13) we see that the function $\mathscr{H}_{(1^*,2^*)}$ and, hence, the function η can be determined through experimental measurements of the amount of heat absorbed during irreversible processes; $\bar{\eta}$ being a quantity which can be experimentally determined by standard calorimetric procedures (cf. [6], p. 83-87). That for each system there must be (to within a constant) only one entropy function η is a consequence of the fact that η is defined through the supremum (5.13).

It is an easy matter to verify that for reversible processes

$$\bar{\eta} \equiv \eta \qquad (5.17)$$

to within a constant, and that, therefore, the entropy η as above defined is a consistent generalization of the reversible entropy $\bar{\eta}$. Indeed, since relation (4.1) implies that for reversible processes the time integral of Q/θ

depends only on the initial and on the final state of the process, it follows
from (5.11) that when 1* and 2* are states of reversible equilibrium the
quantity $\mathcal{H}_{(1,2,1*,2*)}$ does not depend on the states 1 and 2. Consequently,

$$\mathcal{H}_{(1,2,1*,2*)} = \mathcal{H}_{(1*,2*)} = \int_{1*}^{2*} \rho\dot{\eta}dt \qquad (5.18)$$

when reversible processes are considered. From (5.18), from (5.16) and
from the fact that these relations can be applied to any reversible process
whatsoever, it follows that

$$\dot{\overline{\eta}} = \dot{\eta}. \qquad (5.19)$$

Thus relation (5.17) follows to within an inessential constant.

Inequality (5.15) has been deduced as a necessary consequence of the
second principle of thermodynamics. Conversely, by denying (5.15) we
can arrive at a contradiction of postulate (C). To prove this, consider a
system undergoing an infinitesimal process which starts from the state 1*
and ends to the state $\overline{1}*$ in the infinitesimal neighbourhood of 1*. Suppose
that for this process

$$\frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt > \rho\dot{\overline{\eta}}dt \qquad (5.20)$$

in contradiction with (5.15). For this infinitesimal process we have, clearly,
that

$$\frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt \equiv \int_{1*}^{\overline{1}*} \frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt. \qquad (5.21)$$

In view of definition (5.16) we can thus write (5.20) in the form

$$\int_{1*}^{\overline{1}*} \frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt > \mathcal{H}_{(1*,\overline{1}*)}. \qquad (5.22)$$

Let 1 and 2 be two states of reversible equilibrium and consider the cycle
$1* - \overline{1}* - 2 - 1 - 1*$. From (5.13) we have that the quantity $\mathcal{H}_{(1,2,1*,\overline{1}*)}$
relevant to this cycle and defined by (5.11) must be such that

$$\mathcal{H}_{(1,2,1*,\overline{1}*)} \leq \mathcal{H}_{(1*,\overline{1}*)} \qquad (5.23)$$

But from (5.23), (5.22) and from (5.11) it follows that

$$\int_{1*}^{\overline{1}*} \frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt > \int_{1}^{2} \rho\dot{\overline{\eta}}dt - \int_{\overline{1}*}^{2} \frac{Q}{\theta} dt - \int_{1}^{1*} \frac{Q}{\theta} dt. \qquad (5.24)$$

That is

$$\oint \frac{Q}{\theta} dt = \int_{1*}^{\overline{1}*} \frac{1}{\theta}(\text{div } \underset{\sim}{h} + \rho s)dt + \int_{\overline{1}*}^{2} \frac{Q}{\theta} dt + \int_{2}^{1} \rho\dot{\overline{\eta}}dt + \int_{1}^{1*} \frac{Q}{\theta} dt > 0 \quad (5.25)$$

which contradicts (4.5) and (4.6) and, hence, postulate (C). Relation (5.15)
represents, therefore, a mathematical formulation of the second principle,
which is equivalent to formulation (C) for the case of classical single-phase
continua. To assume any other not equivalent form would be the same as

to admitting the possibility of perpetual motions of the second kind (cf. criticism in [8]).

Observe, finally, that the entropy defined by (5.6) is a state function depending on the material making up the system. It is, therefore, a constitutive quantity that has to be determined by appropriate experiments. Accordingly, there are no *a priori* restrictions to the form which the entropy function can assume, provided, of course, that this form fulfils the general requirements of a correct physical description (cf. *e. g.*, the requirements imposed by the principle of material frame-indifference). In some approaches to non-equilibrium thermodynamics, the entropy of the material is expressed as the sum of products of appropriate *forces* and *fluxes*. Whether or not such an expression for the entropy function can be achieved in an unambiguous way for every material, is a problem still debated. This problem, however, is outside of the scope of the present paper, whose aim has been that of establishing a correct local formulation for the second principle of thermodynamics, quite independently of any particular form of the relation expressing the entropy as a function of the state variables of the system. Since the second principle deals with every possible thermodynamic system, there is no reason to exclude any particular form for the entropy function.

It is perhaps worthwhile to stress, moreover, that the approach consistently adopted throughout this paper is the macroscopic one. Of course, this is not the only approach by which the behaviour of a real system can be described. A monoatomic gas, for instance, can be described either by regarding it as a continuous material, or by considering it as composed of a collection of small hard spheres in random motion *(kinetic theory)*. In the first case, we assign the constitutive equations for energy, entropy, stress and heat flux vector. In the second case, we introduce particular hypotheses for the forces the spheres exert on each other and for the statistical distribution of the speed of the spheres. Both the models may lead to consistent results when they are applied to describe the behaviour of the gas in a certain range of processes. Since, however, they originate from different idealizations of the real system, they may lead to discrepant results when applied to the study of processes for which the above idealizations prove to be not equivalent. It is not surprising, therefore, that a constitutive quantity, say the entropy, determined experimentally by considering a monoatomic gas as a continuum, does not generally coincide with the analogous quantity calculated through the kinetic theory. This does not mean that the real gas possesses two different entropies, but merely means that the two mathematical models associated with it are different.

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