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A note on the existence of entropy in classical thermodynamics

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Two new conditions for the existence of entropy for elastic systems are introduced. Both conditions are expressed in terms of some measures of efficiency of cyclic processes. While the first condition employs the notion of crude efficiency introduced by Day, the second condition is a statement about the efficiency in the usual physical sense.

Wprowadzono dwa nowe warunki istnienia entropii dla układów sprężystych. Obydwa warunki wyrażono przez miary sprawności procesów cyklicznych. O ile pierwszy warunek stanowi pojęcie zgrubnej sprawności wprowadzone przez Day'a, to drugi warunek jest sformułowaniem w zwykłym fizycznym sensie.

Выведены два новых условия существования энтропии для упругих систем. Оба условия выражены через меры коэффициента полезного действия циклических процессов. Поскольку первое условие составляет понятие грубого коэффициента полезного действия введенное Деем, постольку второе условие является формулировкой коэффициента полезного действия в обыкновенном физическом смысле.

1. Introduction

In the article [1] Day has exhibited a condition equivalent to the existence of entropy for elastic systems for which the absolute temperature is taken as a primitive concept. Day's condition involves the notion of the Carnot process of the system and of the crude efficiency of a process. The Carnot processes are such processes during which the heat is absorbed and emitted at just one temperature or not at all(1). The crude efficiency of a process is defined to be the number

$$\xi = \frac{h^+}{\theta^+} - \frac{h^-}{\theta^-},$$

where h^+ and h^- denote respectively the heat absorbed and emitted by the system during a process, and θ^+ and θ^- denote respectively the maximum and minimum temperatures at which the heat is absorbed or emitted. If no heat is absorbed or emitted, we define the crude efficiency to be 0.

The main result of [1] is the following assertion(2). The system has entropy if and only if among all processes connecting two given states the Carnot processes have the greatest crude efficiency. Day also states that systems having entropy satisfy the following condition

(1) Note that it does not follow from the definition of a Carnot process that Carnot processes are isothermal: during adiabatic parts the temperature can vary in an arbitrary way.

(2) For a precise statement see Sect. 2.

hereafter denoted as III: the crude efficiency of each cyclic process is not positive. As he notes, it is tempting to conjecture that this condition is also sufficient for the existence of entropy. However, a simple counter-example given in [1] indicates that such a conjecture is false.

The purpose of this note is to show that it is possible to strengthen Condition III in such a way that it becomes really necessary and sufficient for the existence of entropy.

Define a generalized Carnot process as a process during which the heat is absorbed at one constant temperature θ^+ and emitted at a second constant temperature θ^-, where $\theta^+ \geqslant \theta^-$. It can be shown (see Sect. 3) that if the system has entropy, then the crude efficiency of each cyclic generalized Carnot process is 0. Thus the system which has entropy satisfies the following condition (hereafter denoted as III'): the crude efficiency of each cyclic process is not positive and the crude efficiency of each cyclic generalized Carnot process is 0.

The main result of Sect. 3 is the assertion that the system discussed has entropy if and only if it satisfies the condition III'.

Condition III' has the advantage that it can be easily reformulated as a statement about the real efficiency of cyclic processes, defined as the ratio of the total work done by the system to the heat absorbed by that system during the cylic process. In fact, the total work w done during a cyclic process is the difference between the heat absorbed and the heat emitted,

$$w = h^+ - h^-.$$

In classical thermodynamics the real efficiency μ is defined as

$$\mu = \frac{w}{h^+} = \frac{h^+ - h^-}{h^+}.$$

The condition $\xi \leqslant 0$ may then be rewritten (see Sect. 4) as

$$\mu \leqslant \frac{\theta^+ - \theta^-}{\theta^+}$$

and similarly the condition $\xi = 0$ as

$$\mu = \frac{\theta^+ - \theta^-}{\theta^+}.$$

Accordingly, the new condition of the existence of entropy may be reformulated as follows. The system has entropy if and only if real efficiency of each cyclic process satisfies $\mu \leqslant \frac{\theta^+ - \theta^-}{\theta^+}$ and real efficiency of each cyclic generalized Carnot process satisfies $\mu = \frac{\theta^+ - \theta^-}{\theta^+}$.

The fact that entropy is derivable from the physically plausible conditions on the real efficiency given above seems to have significance for the axiomatic development of thermodynamics.

2. Basic concepts and results of [1]

The basic mathematical structure underlying considerations in the following sections is the same as in [1]. For our purposes, *the thermodynamical system*, or simply a *system*, is defined by two continuous mappings θ and σ, defined on an open and connected subset U of some finite-dimensional inner product space V and with values in $\mathsf{R}^{++} = (0, \infty)$ and V, respectively:

$$\theta: \quad U \to \mathsf{R}^{++},$$
$$\sigma: \quad U \to V.$$

The subset U of V is called the *state space* of the system and its elements $x, y, \ldots$ are called *states*. The values $\theta(x)$ and $\sigma(x)$ of the mappings θ and σ are called the *temperature* and the *generalized stress* of the state x. The term *process* will denote any function f mapping a non-degenerate interval $[0, d_f]$ into the set U which is continuous and piecewise continuously differentiable. The number $d_f > 0$ will be called the *duration* of the process and the values $f^I = f(0)$ and $f^F = f(d_f)$ will be refered to as the *initial* and *final values* of the process. For each $t \in [0, d_f]$, for which $\dot{f}(t)$ exists, the value

$$q(t) = \sigma(f(t)) \cdot \dot{f}(t) \tag{2.1}$$

will be called the rate of heat supply at time t during the process f. The quantity $h(f)$,

$$h(f) = \int_0^{d_f} \sigma(f(t)) \cdot \dot{f}(t)\, dt$$

is then the total heat absorbed by the system during the process f.

An example of a system is provided by an *elastic fluid*. The state x is completely determined by the specific internal energy e and by the specific volume v, $x = (e, v)$; the pressure p and temperature θ are determined by "equations of state"

$$\theta = \theta(e, v), \quad p = p(e, v). \tag{2.2}$$

In this case the inner product space V is identified with R^2, the set of all pairs of real numbers, and the state space U with the set of all possible values of e and v. Of course, the mapping θ of Eqs. (2.2) is identified with the mapping θ in the definition of a system. According to this definition, σ has to map U into V, i.e. the subset of R^2 into R^2, but function p maps U into R. Define $\sigma(x) = \sigma(e, v)$ as

$$\sigma(x) = \sigma(e, v) = (1, p(e, v)) \in \mathsf{R}^2.$$

The definition of the rate of heat supply, Eq. (2.1), then gains the familiar form of the First Law of Thermodynamics

$$q(t) = \dot{e}(t) + p(e(t), v(t)) \cdot \dot{v}(t),$$

where $f(t) = (e(t), v(t))$ is a process of the system.

We now turn back to general systems defined at the beginning of this section.

Let $x, y \in U$ and f be a process. If $f^I = x$ and $f^F = y$, then the process is said to *connect x to y* and we write $P(x, y)$ for the set of all processes connecting x to y. The process is said to be *cyclic* if $f^I = f^F$. If $f \in P(x, y)$, then the *time-reversal* of f will be defined as the process $\bar{f} \in P(y, x)$ of duration d_f, for which

$$\bar{f}(t) = f(d_f - t) \quad \text{for each} \quad t \in [0, d_f].$$

If $x, y, z \in U$, f $P(x, y)$ and $g \in P(y, z)$, then the *continuation of f with g* will be defined as the process $f \divideontimes g \in P(x, z)$ of duration $d_f + d_g$, for which

$$(f \divideontimes g)(t) = \begin{cases} f(t) & \text{if} \quad t \in [0, d_f] \\ g(t - d_f) & \text{if} \quad t \in [d_f, d_f + d_g]. \end{cases}$$

Following Day, we define for each process f

(1) the *set of all times at which the heat is absorbed* and the *set of all times at which the heat is emitted* during f respectively, by

$$t^+(f) = \{t \in [0, d] \| \dot{f}(t) \quad \text{is defined and} \quad \sigma(f(t)) \cdot \dot{f}(t) > 0\},$$
$$t^-(f) = \{t \in [0, d] \| \dot{f}(t) \quad \text{is defined and} \quad \sigma(f(t)) \cdot \dot{f}(t) < 0\};$$

(2) the *heat absorbed on f* and the *heat emitted on f* respectively, by

$$h^+(f) = \int_{t^+(f)} \sigma(f(t)) \cdot \dot{f}(t) dt \geqslant 0,$$

$$h^-(f) = -\int_{t^-(f)} \sigma(f(t)) \cdot \dot{f}(t) dt \geqslant 0.$$

If $t^+(f) = t^-(f) = \emptyset$, then the process is said to be *adiabatic*. If f is not adiabatic, we then define the *maximum* and *minimum temperatures at which heat is absorbed or emitted on f* by

$$\theta^+(f) = \sup\{\theta(f(t)) | t \in t^+(f) \cup t^-(f)\},$$
$$\theta^-(f) = \inf\{\theta(f(t)) | t \in t^+(f) \cup t^-(f)\},$$

respectively, in the same way as in [1].

Following Day we then define the crude efficiency of the process f to be the number $\xi(f)$ where

$$\xi(f) = \frac{h^+(f)}{\theta^+(f)} - \frac{h^-(f)}{\theta^-(f)}$$

if f is not adiabatic, and $\xi(f) = 0$ if f is adiabatic.

We now give a precise definition of a notion of a generalized Carnot process as mentioned in Sect. 1. A process f is said to be a *generalized Carnot process* if there are two positive numbers θ^+ and θ^- with $\theta^+ \geqslant \theta^-$ such that

$$t \in t^+(f) \Rightarrow \theta(f(t)) = \theta^+,$$
$$t \in t^-(f) \Rightarrow \theta(f(t)) = \theta^-.$$

This means either that f is adiabatic or that $\theta(f(t)) = \theta^+(f) = \theta^+$ for $t \in t^+(f)$ and $\theta(f(t)) = \theta^-(f) = \theta^-$ for $t \in t^-(f)$. Note that, generally, the time reversal of a generalized Carnot process is not a generalized Carnot process. The concept of a generalized Carnot process is a generalization of the concept of a Carnot process introduced in [1]. A process is said to be a *Carnot process* if there is a number α such that $\theta(f(t)) = \alpha$ for each $t \in t^+(f) \cup t^-(f)$. This means that either f is adiabatic or that $\theta^+(f) = \theta^-(f) = \alpha$. The set of all Carnot processes connecting x to y will be denoted by $C(x, y)$. It is a straightforward matter to verify that if $f \in C(x, y)$, then $\bar{f} \in C(y, x)$ and $\xi(\bar{f}) = -\xi(f)$. In the subsequent sections we shall also need the following special type of Carnot processes: Carnot process is said to be a *monotonous Carnot process* if either $t^+(f) = \emptyset$ or $t^-(f) = \emptyset$. Each adiabatic process is a monotonous Carnot process. The set of all monotonous Carnot processes connecting x to y will be denoted by $C_0(x, y)$. If $f \in C_0(x, y)$, then $\bar{f} \in C_0(y, x)$.

In the remaining part of this section we shall state precisely Day's results mentioned in Section 1. The main result concerning the necessary and sufficient condition for the existence of entropy requires a mild restriction C on the system:

C. *If $x, y \in U$, and $\alpha \in \theta(U)$, then there is a Carnot process $g \in P(x, y)$ such that* $\theta^+(g) = \theta^-(g) = \alpha$.

Day's THEOREM. *Suppose that C holds. Then the following conditions* I *and* II *are equivalent*:

I. *If $x, y \in U$, $f \in P(x, y)$ and $g \in C(x, y)$, then $\xi(f) \leqslant \xi(g)$.*

II. *There is a smooth scalar field η: $U \to \mathrm{R}$ such that*

$$\sigma = \theta \nabla \eta.$$

Day's Theorem has the following corollary also stated in [1]:

COROLLARY to Day's Theorem. *Suppose that C holds. Then, Condition* I (*and hence also* II) *implies* III:

III. *If f is any cyclic process, then $\xi(f) \leqslant 0$.*

3. Conditions equivalent to the existence of entropy

The following technical assumption about the system will be appropriate for our purposes:

C′. *If $x, y \in U$ and $\alpha \in \theta(U)$, then there is a monotonous Carnot process $g \in C_0(x, y)$ such that for every $t \in t^+(g) \cup t^-(g)$ we have $\theta(g(t)) = \alpha$.*

This axiom says that any two states may be connected by a process which is either adiabatic or such that the heat is only absorbed or only emitted during that process at a prescribed constant temperature. Note that C' does not imply C, since C requires that each of the two states be connected by a Carnot process g which is not adiabatic and which satisfies $\theta^+(g) = \theta^-(g) = \alpha$.

Now we are able to state and prove the main result of this note.

THEOREM. *If C′ holds, then* I, II, *and* III′ *are equivalent*:

I. *If $x, y \in U$, $f \in P(x, y)$ and $g \in C(x, y)$, then $\xi(f) \leqslant \xi(g)$.*

II. *There is a smooth scalar field η: $U \to \mathrm{R}$ such that*

$$\sigma = \theta \nabla \eta.$$

III′. *If f is a cyclic process, then $\xi(f) \leqslant 0$; if, moreover, f is a generalized Carnot process, then $\xi(f) = 0$.*

Proof. It suffices to show the following three implications: $\mathrm{I} \Rightarrow \mathrm{II}$, $\mathrm{II} \Rightarrow \mathrm{III}'$, and $\mathrm{III}' \Rightarrow \mathrm{I}$.

Now, the proof of $\mathrm{I} \Rightarrow \mathrm{II}$ may be accomplished in a very similar way as that of $\mathrm{I} \Rightarrow \mathrm{II}$ in the Proof of Day's Theorem (see p. 163 in [1]). Note that our conditions I and II are completely identical respectively with the conditions I and II in [1]. However, for our purposes Day's proof must be slightly modified since the author uses in his proof the condition C, while we have at hand our C'. Such a modification is only a technical matter and this is why the proof of I $\Rightarrow$ II is omitted here.

Proof of II $\Rightarrow$ III′. The fact that Condition II implies $\xi(f) \leqslant 0$ for each cyclic process f is proved in [1][3]. Hence it remains to be shown that if the system has entropy, then each cyclic generalized Carnot process satisfies $\xi(f) = 0$. Let f be a cyclic generalized Carnot process. First, if f is adiabatic, then by the very definition of ξ, one has $\xi(f) = 0$. Next, suppose that f is not adiabatic. Observe then that

for all $t \in t^+(f)$

$$\theta(f(t)) = \theta^+(f) \tag{3.1}$$

and for all $t \in t^-(f)$

$$\theta(f(t)) = \theta^-(f). \tag{3.2}$$

The steps in the following computation follows from Eqs. (3.1), (3.2), from the definitions of $h^+(f)$ and $h^-(f)$, from the existence of entropy, and from $f^F = f^I$:

$$\xi(f) = \frac{h^+(f)}{\theta^+(f)} - \frac{h^-(f)}{\theta^-(f)} = \int\limits_{t^+(f)} \frac{\sigma(f(t))\cdot\dot{f}(t)}{\theta^+(f)}\,dt + \int\limits_{t^-(f)} \frac{\sigma(f(t))\cdot\dot{f}(t)}{\theta^-(f)}\,dt$$

$$= \int\limits_{t^+(f)} \frac{\sigma(f(t))\cdot\dot{f}(f)}{\theta(f(t))}\,dt + \int\limits_{t^-(f)} \frac{\sigma(f(t))\cdot\dot{f}(f)}{\theta(f(t))}\,dt = \int\limits_0^{d_f} \frac{\sigma(f(t))\cdot\dot{f}(t)}{\theta(f(t))}\,dt$$

$$= \int\limits_0^{d_f} \nabla\eta(f(t))\cdot\dot{f}(t)\,dt = \int\limits_0^{d_f} \frac{d}{dt}[\eta(f(t))]\,dt = \eta(f^F) - \eta(f^I) = 0,$$

i.e. $\xi(f) = 0$.

To show III′ $\Rightarrow$ I, three preliminary results stated in Lemmas 1, 2, and 3 are needed. *From now on till the end of the Proof of Theorem we suppose that C' and* Condition III′ *hold.*

LEMMA 1. *Let $x, y \in U$. Then, either*

(a) *for all $g \in C_0(x, y)$ we have $h^+(g) > 0$, or*

(b) *for all $g \in C_0(x, y)$ we have $h^+(g) = h^-(g) = 0$, or*

(c) *for all $g \in C_0(x, y)$ we have $h^-(g) > 0$.*

Proof. It suffices to show the following implications:

(i_1): $g_1, g_2 \in C_0(x, y)$, $h^+(g_1) > 0 \Rightarrow h^+(g_2) > 0$.

(i_2): $g_1, g_2 \in C_0(x, y)$, $h^-(g_1) > 0 \Rightarrow h^-(g_2) > 0$.

In fact, (i_1) says that if for some g in $C_0(x, y)$ the inequality $h^+(g) > 0$ holds, then this inequality holds for all g in $C_0(x, y)$. Similarly, (i_2) says that if for some g in $C_0(x, y)$ the inequality $h^-(g) > 0$ holds, then this inequality holds for all g in $C_0(x, y)$. As a consequence of (i_1) and (i_2) we have the following. If there is a g in $C_0(x, y)$ which is adiabatic;

[3] In this proof Day does not use Condition C.

then all g in $C_0(x, y)$ are adiabatic since the inequality $h^+(g') > 0$ for some g' in $C_0(x, y)$ contradicts (i_1) and the inequality $h^-(g') > 0$ for some g in $C_0(x, y)$ contradicts (i_2).

(i_1). Suppose that there exists a pair such that $g_1, g_2 \in C_0(x, y)$ and $h^+(g_1) > 0$ and $h^+(g_2) = 0$. Then $\bar{g}_2 * g_1$ is not adiabatic and therefore

$$\xi(\bar{g}_2 * g_1) = \frac{h^+(\bar{g}_2 * g_1)}{\theta^+(\bar{g}_2 * g_1)} - \frac{h^-(\bar{g}_2 * g_1)}{\theta^-(g_2 * g_1)} = \frac{h^-(g_2) + h^+(g_1)}{\theta^+(\bar{g}_2 * g_1)} - \frac{h^+(g_2) + h^-(g_1)}{\theta^-(\bar{g}_2 * g_1)} = \frac{h^-(g_2) + h^+(g_1)}{\theta^+(\bar{g}_2 * g_1)} > 0. \tag{3.3}$$

(Here we have used the fact that by hypothesis $h^+(g_2) = 0$ and also that $h^-(g_1) = 0$ since $h^+(g_1) > 0$ and g_1 is a monotonous Carnot process). But $\bar{g}_2 * g_1$ is cyclic and therefore, according to Condition III′, $\xi(\bar{g}_2 * g_1) \leqslant 0$ which contradicts Eq. (3.3).

(i_2). Suppose that there exists a pair $g_1, g_2 \in C_0(x, y)$ such that $h^-(g_1) > 0$ and $h^-(g_2) = 0$. Similarly, we can show as above that the cyclic process $\bar{g}_1 * g_2$ satisfies

$$\xi(\bar{g}_1 * g_2) = \frac{h^-(g_1) + h^+(g_2)}{\theta^+(\bar{g}_1 * g_2)} > 0,$$

which contradicts Condition III′; q.e.d.

LEMMA 2. *Let $x, y \in U$ and $g_1, g_2 \in C_0(x, y)$. Then, $\xi(g_1) = \xi(g_2)$.*

Proof. By Lemma 1, there are three possibilities:

(a) $h^+(g_1) > 0, \quad h^+(g_2) > 0,$

(b) $h^+(g_1) = h^-(g_1) = h^+(g_2) = h^-(g_2) = 0,$

(c) $h^-(g_1) > 0, \quad h^-(g_2) > 0.$

First, let us consider the case (a). Suppose without any loss of generality that $\theta^+(g_1) \geqslant \theta^+(g_2)$. It then follows that $\theta^+(g_1 * \bar{g}_2) = \theta^+(g_1)$, $\theta^-(g_1 * \bar{g}_2) = \min\{\theta^-(g_1), \theta^-(\bar{g}_2)\} = \min\{\theta^+(g_1), \theta^+(\bar{g}_2)\} = \min\{\theta^+(g_1), \theta^+(g_2)\} = \theta^+(g_2)$.

Moreover, g_1 and g_2 are monotonous Carnot processes and (a) holds; hence $h^-(g_1) = h^-(g_2) = 0$. The above particular results then justify the following computation:

$$\xi(g_1 * \bar{g}_2) = \frac{h^+(g_1 * \bar{g}_2)}{\theta^+(g_1 * g_2)} - \frac{h^-(g_1 * \bar{g}_2)}{\theta^-(g_1 * \bar{g}_2)} = \frac{h^+(g_1) + h^-(g_2)}{\theta^+(g_1)} - \frac{h^-(g_1) + h^+(g_2)}{\theta^+(g_2)} = \frac{h^+(g_1)}{\theta^+(g_1)} - \frac{h^+(g_2)}{\theta^+(g_2)} = \xi(g_1) - \xi(g_2).$$

As $g_1 * \bar{g}_2$ is a cyclic generalized Carnot process, we must have, according to Condition III′, $\xi(g_1 * \bar{g}_2) = 0$ and, consequently, $\xi(g_1) = \xi(g_2)$. In the case (b) the processes g_1 and g_2 are adiabatic and therefore $\xi(g_1) = \xi(g_2) = 0$. In the case (c), assume as in the case (a) that $\theta^+(g_1) \geqslant \theta^+(g_2)$. Similarly as in the case (a) we can show that the cyclic generalized Carnot process $\bar{g}_1 * g_2$ satisfies $0 = \xi(\bar{g}_1 * g_2) = \xi(g_2) - \xi(g_1)$ and hence that $\xi(g_1) = \xi(g_2)$; q.e.d.

LEMMA 3. *If $x, y \in U$, $f \in P(x, y)$ and $g \in C_0(x, y)$, then $\xi(f) \leqslant \xi(g)$.*

Proof. As in the proof of Lemma 2, we consider the three possibilities (a), (b), and (c), stated in Lemma 1. In the case (a) f is not adiabatic, hence $\theta^-(f)$ is defined. By the axiom C' there is a $g' \in C_0(x, y)$ such that $t \in t^+(g') \cup t^-(g') \Rightarrow \theta(g'(t)) = \theta^-(f)$. It follows that $\theta^+(g') = \theta^-(g') = \theta^-(f)$,

$$\theta^+(f*\bar{g}') = \max\{\theta^+(f), \theta^+(\bar{g}')\} = \max\{\theta^+(f), \theta^+(g')\} = \max\{\theta^+(f), \theta^-(\bar{f})\} = \theta^+(f),$$
$$\theta^-(f*\bar{g}') = \min\{\theta^-(f), \theta^-(\bar{g}')\} = \min\{\theta^-(f), \theta^-(g')\} = \min\{\theta^-(f), \theta^-(f)\} = \theta^-(f).$$

Moreover, as g' is a monotonous Carnot process and $h^+(g') > 0$, we have $h^-(g') = 0$. The steps in the following computation then follow from the above relations:

$$\xi(f*\bar{g}) = \frac{h^+(f*\bar{g}')}{\theta^+(f*\bar{g}')} - \frac{h^-(f*\bar{g}')}{\theta^-(f*\bar{g}')} = \frac{h^+(f)+h^-(g')}{\theta^+(f)} - \frac{h^-(f)+h^+(g')}{\theta^-(f)}$$
$$= \frac{h^+(f)}{\theta^+(f)} - \frac{h^-(f)}{\theta^-(f)} - \frac{h^+(g')}{\theta^+(g')} = \xi(f) - \xi(g').$$

Now $f*\bar{g}'$ is a cyclic process and hence by Condition III', $\xi(f*\bar{g}') \leqslant 0$; consequently $\xi(f) \leqslant \xi(g')$. By Lemma 2, $\xi(g) = \xi(g')$, therefore also $\xi(f) \leqslant \xi(g)$. Next, turn to the case (b). Then each $g \in C_0(x, y)$ must be adiabatic and a straightforward computation shows that $\xi(f*\bar{g}) = \xi(f)$. As $f*\bar{g}$ is cyclic, we have $\xi(f) = \xi(f*\bar{g}) \leqslant 0$; but since g is adiabatic, $\xi(g) = 0$ and hence $\xi(f) \leqslant \xi(g)$. Finally, consider case (c). Similarly as in the case (a) there is a process $g' \in C_0(x, y)$ such that $h^-(g') > 0$ and $\theta^+(g') = \theta^-(g') = \theta^+(f)$. The process $f*\bar{g}'$ then satisfies $\xi(f*\bar{g}') = \xi(f) - \xi(g')$ and since $f*\bar{g}'$ is cyclic, we have $\xi(f*\bar{g}') \leqslant 0$. Consequently, $\xi(f) \leqslant \xi(g')$ and by Lemma 2 also $\xi(f) \leqslant \xi(g)$; q.e.d.

Now, after proving necessary preliminary results, it is not difficult to complete the proof of the Theorem. Suppose that $f \in P(x, y)$, $g \in C(x, y)$. Our aim is to prove the inequality $\xi(f) \leqslant \xi(g)$. To this end let us choose arbitrary $g' \in C_0(x, y)$. By Lemma 3 then $\xi(g) \leqslant \xi(g')$. Now since $\bar{g}' \in C_0(y, x)$, $\bar{g} \in C(y, x)$, we must also have $\xi(\bar{g}) \leqslant \xi(\bar{g}')$. Using the relations $\xi(\bar{g}) = -\xi(g)$, $\xi(\bar{g}') = -\xi(g')$ which hold for all Carnot processes, we obtain from $\xi(\bar{g}) \leqslant \xi(\bar{g}')$ the inequality $\xi(g') \leqslant \xi(g)$ which together with the inequality $\xi(g) \leqslant \xi(g')$ yields $\xi(g) = \xi(g')$. As $f \in P(x, y)$, $g' \in C_0(x, y)$, we have by Lemma 3 the inequality $\xi(f) \leqslant \xi(g')$ and, consequently, $\xi(f) \leqslant \xi(g)$; q.e.d.

4. Real efficiency of cyclic processes

Let us define for each cyclic process f the *work done by the system during that process* by

$$w(f) = \int_0^{d_f} \sigma(f(t)) \cdot \dot{f}(t)\, dt.$$

Using the definitions of $h^+(f)$ and $h^-(f)$, we obtain, as we should expect, that the work done during the process f is the difference between the heat absorbed and the heat emitted during f:

$$w(f) = h^+(f) - h^-(f).$$

In classical thermodynamics the real efficiency $\mu(f)$ of a non-adiabatic cyclic process f is defined as the ratio of the work done by the system to the heat absorbed by it:

$$\mu(f) = \frac{w(f)}{h^+(f)} = \frac{h^+(f) - h^-(f)}{h^+(f)}.$$

In contrast to the functional ξ, the functional μ has a direct physical significance.

The inequality $\xi(f) \leqslant 0$ means, for non-adiabatic processes f, that

$$\frac{h^+(f)}{\theta^+(f)} - \frac{h^-(f)}{\theta^-(f)} \leqslant 0,$$

or, equivalently,

$$-\frac{h^-(f)}{h^+(f)} \leqslant -\frac{\theta^-(f)}{\theta^+(f)}$$

and

$$1-\frac{h^-(f)}{h^+(f)} \leqslant 1-\frac{\theta^-(f)}{\theta^+(f)}.$$

Now the left-hand side of the last inequality is just the real efficiency of the process f, and hence

$$\mu(f) \leqslant \frac{\theta^+(f)-\theta^-(f)}{\theta^+(f)}.$$

Similarly, equation $\xi(f) = 0$ may be rewritten for non-adiabatic processes as

$$\mu(f) = \frac{\theta^+(f)-\theta^-(f)}{\theta^+(f)}.$$

Hence, Condition III′ may be now reformulated in terms of the functional μ as follows:

IV. *If f is non-adiabatic and cyclic, then*

$$\mu(f) \leqslant \frac{\theta^+(f)-\theta^-(f)}{\theta^+(f)}$$

and if, moreover, f is a generalized Carnot process, then

$$\mu(f) = \frac{\theta^+(f)-\theta^-(f)}{\theta^+(f)}.$$

To summarize the above considerations, we have shown that III′ $\Rightarrow$ IV. Conversely, it is possible to show that IV $\Rightarrow$ III′: For non-adiabatic processes it is sufficient to proceed in an opposite way as above. If f is adiabatic, then $\xi(f) = 0$ and hence also $\xi(f) \leqslant 0$. That is, we have:

R e m a r k. *Conditions* III′ *and* IV *are equivalent.*

Condition IV says that among all cyclic and non-adiabatic processes with the maximal temperature θ^+ and the minimal temperature θ^- ($\theta^+ \geqslant \theta^-$) the generalized Carnot processes give the greatest value of the real efficiency and that this value is $\frac{\theta^+-\theta^-}{\theta^+}$. Note that this proposition generalizes Carnot's discovery that in an ideal gas the cyclic processes consisting of two adiabatics and two isotherms with the temperatures θ^+ and θ^- have the real efficiency equal to $\frac{\theta^+-\theta^-}{\theta^+}$.

Implication II $\Rightarrow$ IV (which holds according to the Theorem and the Remark) then shows that if the existence of entropy is postulated, then the class of all processes with the efficiency $\frac{\theta^+-\theta^-}{\theta^+}$ is broader, namely, that it contains all generalized Carnot processes with corresponding temperatures. Moreover, it may also be shown that in the case of the existence of entropy the generalized Carnot processes are the only processes with the efficiency $\frac{\theta^+ - \theta^-}{\theta^+}$.

Implication IV $\Rightarrow$ II has an important physical significance: it says that entropy is derivable from a physically plausible postulate IV.

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