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Proof that the Clausius-Serrin inequality is equivalent to a strengthened "Kelvin's law"

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Fisica matematica (Termodinamica). — *Proof that the Clausius-Serrin inequality is equivalent to a strengthened "Kelvin's law"*. Nota di CHI-SING MAN, presentata (*) dal Socio straniero C. TRUESDELL.

RIASSUNTO. — A partire da una formulazione precisa della «disuguaglianza di Clausius» per i processi ciclici, in termini della funzione di accumulazione di Serrin, viene data una dimostrazione matematica esatta del fatto che la disuguaglianza di Clausius correttamente formulata (ovvero la disuguaglianza di Clausius-Serrin) è equivalente a una versione rafforzata della «legge di Kelvin». L'introduzione di un gas ideale con calore specifico costante fornisce alla dimostrazione qui presentata una notevole semplicità ed eleganza. Lo strumento matematico usato non richiede più della convergenza uniforme e delle proprietà elementari dell'integrale di Riemann-Stieltjes.

§ 1. The "Clausius inequality" for cyclic processes has lost its mystic quality ever since Serrin ([1], [2]) introduced his accumulation function. The accumulation function $C_P(\cdot)$ of a thermodynamic process P has the following physical meaning: the value $C_P(\theta)$ of C_P at the ideal-gas temperature (1) θ is the heat gained at temperatures $\leq \theta$ by the body $\mathscr{B}$ in question during the process P; the difference $C_P(\theta_2) - C_P(\theta_1)$, in which $\theta_1 < \theta_2$, equals the heat gained at temperatures $\theta \in (\theta_1, \theta_2]$ by $\mathscr{B}$ during P. In continuum thermodynamics we can show that $C_P(\cdot)$ has the following properties: (*i*) $C_P(\cdot)$ is a right-continuous function of bounded variation on $(0, \infty)$; (*ii*) $C_P(\theta) = 0$ for all $\theta < \theta^P_{\min}$; (*iii*) $C_P(\theta) = \bar{C}$ for all $\theta \geq \theta^P_{\max}$; here $\bar{C}$ is the total gain of heat, $\theta^P_{\min}$ and $\theta^P_{\max}$ denote the infimum and the supremum, respectively, of the temperatures experienced by some body point in $\mathscr{B}$ during the process P, and $\theta^P_{\min} > 0$, $\theta^P_{\max} < \infty$ by assumption. (Cf. Man [3]). Hereinafter it is understood that $C_P(\cdot)$ has these mathematical properties for every thermodynamic process P. The reader who intends to interpret what follows as something within an abstract framework broader than continuum thermodynamics should take the foregoing assertion as a postulate.

The "Clausius inequality" for cyclic processes (2) can be stated precisely

(*) Nella seduta del 6 dicembre 1980.

(1) Serrin defined his accumulation function on the hotness manifold $\mathscr{H}$. Here I assume that ideal-gas temperature furnishes a global empirical temperature scale which maps $\mathscr{H}$ onto $(0, \infty)$, and I take $C_P(\cdot)$ as defined over the ideal-gas temperatures $\theta \in (0, \infty)$.

(2) Regarding the definition of cyclic processes, in this paper we have two options: (I.) "Cyclic process" is taken as a primitive concept, but we agree that equilibrium processes, Carnot processes and reversed Carnot processes executed by a body of ideal gas, to be defined below, are cyclic. (II.) We assume that for every body $\mathscr{B}$ there is a state space $\Sigma_{\mathscr{B}}$ associated with $\mathscr{B}$ and a set $\Pi_{\mathscr{B}}$ of processes open to $\mathscr{B}$. Each $P \in \Pi_{\mathscr{B}}$ is a map with codomain $\Sigma_{\mathscr{B}}$ and domain $[0, d_P]$, for some $d_P > 0$ called the duration of P. A process $\bar{P}$ executed by $\mathscr{B}$ in the interval of time $[t_1, t_2]$ is a map from $[t_1, t_2]$ to $\Sigma_{\mathscr{B}}$ such that $\bar{P}(t) = P(t - t_1)$, for some

in terms of the accumulation function as follows [(3)]:

(C—S). For every cyclic process P, $\int_0^\infty \theta^{-1}\,dC_P \leq 0$.

The integral in (C—S) makes sense as an improper Riemann-Stieltjes integral: for every interval $[\theta_a, \theta_b]$, the Riemann-Stieltjes integral $\int_{\theta_a}^{\theta_b} \theta^{-1}\,dC_P$ exists because θ^{-1} is continuous and $C_P(\cdot)$ is of bounded variation on $[\theta_a, \theta_b]$; $\int_0^\infty \theta^{-1}\,dC_P = \int_{\theta_a}^{\theta_b} \theta^{-1}\,dC_P$ for all $\theta_a < \theta^P_{\min} \leq \theta^P_{\max} < \theta_b$. Although Clausius, lacking the appropriate mathematical apparatus, was unable to formulate his inequality precisely, (C—S) does seem to capture exactly what he had in mind. (Cf. Clausius [5], § 1.) Because it was Clausius who first suggested, albeit vaguely and imprecisely, the physical ideas to be captured precisely by (C—S), and because it was Serrin who in effect first wrote (C—S) down as a clear and specific assertion (cf. footnote (3)), it seems fair to name the assertion (C—S) after Clausius and Serrin and call it the Clausius-Serrin inequality.

$P \in \Pi_{\mathscr{B}}$ of duration $t_2 - t_1$. $\overline{P}$ is defined as cyclic if it starts and ends at the same state, i.e., $\overline{P}(t_1) = \overline{P}(t_2) = \sigma \in \Sigma_{\mathscr{B}}$. Man [4] discards (I.) and adopts (II.) in discussing systems with approximate restorability.

(3) By expressing (C—S) in terms of the Borel measure on the hotness manifold generated by the accumulation function, Serrin in effect first wrote it down as a conjecture in his abstract thermodynamic theory (cf. Serrin [1], p. 427, footnote). Later Serrin [2] seemed to prefer a more general formulation—there he propounded a new inequality, namely, "the genera accumulation inequality", which is potentially more general than (C—S) because $C_P(\cdot)$ need not be a function of bounded variation for that inequality to be defined. On the other hand, if $C_P(\cdot)$ satisfies (*i*), (*ii*) and (*iii*) above, (C—S) is in fact equivalent to the general accumulation inequality of Serrin [2] because

$$\int_0^\infty \frac{1}{\theta}\,dC_P = \lim_{\substack{\theta_b \to \infty \\ \theta_a \to 0}} \left(\left[\frac{1}{\theta} C_P \right]_{\theta_a}^{\theta_b} - \int_{\theta_a}^{\theta_b} C_P\,d\left(\frac{1}{\theta}\right) \right) = \int_0^\infty \frac{C_P(\theta)}{\theta^2}\,d\theta .$$

When restricted to continuum thermodynamics, Serrin's two formulations and (C—S) are equivalent statements. Here I prefer (C—S) as it stands to both of Serrin's formulations because by avoiding the language of measure theory it is mathematically more elementary than Serrin's first formulation, and by retaining a formal resemblance to Clausius's original inequality (C—S) not only lays bare its own historical roots but also lends itself a more direct physical interpretation than the general accumulation inequality. Of course my choice here is just a matter of taste—one could also prefer with good reason the accumulation inequality both for its generality and because it does not involve Stieltjes integration.

While Clausius thought that his inequality did " express the second principle analytically in its simplest form ", certainly no one could ever provide a logically tight proof that something so ill formulated as that and the equally vague classical statements of the Second Law as assertions of impossibility were indeed equivalent. The clear and specific assertion (C—S), on the other hand, is susceptible of proof or disproof. Thus it is now reasonable to ask whether (C—S) be equivalent to any of the classical statements in some precise interpretation. In his Muncie lectures (4) Serrin proved " the general accumulation inequality " equivalent to the following proposition: (5)

(S). The accumulation function $C(\cdot)$ of a cyclic process cannot have the form: $\bar{C} > 0$ and $C(\theta) \geq 0$ for all θ. ($\bar{C}$ is the total gain of heat).

This is tantamount to say that (C—S) is equivalent to (S). (Cf. footnote (3).) While Serrin's proposition (S) is itself a statement of impossibility, it seems also desirable to seek a statement which sounds close to one of the classical statements, retains their intuitive appeal, and is equivalent to (C—S), thus lending it some further intuitive support.

The object of this paper is to show that (C—S) is indeed equivalent to a strengthened version of " Kelvin's law ". For simplicity and elegance, we shall assume in the proof the existence of an ideal gas with constant specific heats. (6) The significance of that equivalence is discussed in the last section of the paper.

§ 2. Kelvin's original statement of the Second Law ([8], § 12) is inscrutable:

> It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

What follows is a sample of what has come down in the tradition of modern textbooks as " Kelvin's law " (cf. Pippard [9], p. 30), a statement usually also taken as the denial of the possibility of " perpetual motion of the second kind ":

> It is impossible to devise an engine which, working in a cycle, shall produce no effect other than the extraction of heat from a reservoir and the performance of an equal amount of mechanical work.

(4) Lectures given at the NSF-CBMS Regional Conference on the Mathematical Foundations of Thermodynamics (July 16–21, 1978), Ball State University, Muncie, Indiana.

(5) In the proof (due to J. Serrin and R. Hummel) he presented at Muncie, Serrin used the assumption that there is a body of ideal gas. (I refer here to the notes I took when attending those lectures.) In the summer of 1979 I learned that that proof was simplified by D. Owen. Cf. Serrin ([2], p. 369) for information about other proofs.

(6) The equivalence still holds if instead of this assumption we adopt a variant of the thermometric postulate of Serrin [6]. Cf. Man [7].

Assuming the validity of the First Law, Serrin [2] used the accumulation function to give " Kelvin's law " a mathematical interpretation:

(K). The accumulation function $C(\cdot)$ of a cyclic process cannot have the form:

$$C(\theta) = \begin{cases} 0\,, & \text{if } \theta < \theta_0 \\ \alpha\,, & \text{if } \theta \geq \theta_0 \end{cases}, \qquad \text{for some } \alpha > 0, \text{ and for some } \theta_0 > 0\,.$$

If we introduce the Heaviside function

$$h(x) = \begin{cases} 0\,, & \text{if } x < 0 \\ 1\,, & \text{if } x \geq 0 \end{cases},$$

and use the same notation $h(\theta - \theta_0)$ to denote the restriction of the latter to $(0, \infty)$, (K) forbids any cyclic process to have an accumulation function in the class $\mathscr{F} \equiv \{f \in \mathrm{R}^{(0,\infty)} : f(\theta) = \alpha h(\theta - \theta_0),$ for some $\alpha > 0\,, \theta_0 > 0\}$. Here $\mathrm{R}^{(0,\infty)}$ stands for the set of all functions from $(0, \infty)$ to the reals R.

Is (K) equivalent to (C—S)? It is obvious that (C—S) implies (K). But is (K) strong enough to imply (C—S)? Probably not. As we shall see, however, provided there is an ideal gas with constant specific heats, we can find a statement, which we may call (K_s), that is equivalent to (C—S) and may be taken as a strengthened version of (K).

Before stating (K_s) let us introduce some notations and definitions. Let *Cyc* denote the subset of real-valued functions on $(0,\infty)$ defined by the following property: $f \in Cyc$ if and only if f is the accumulation function of some cyclic process. (7) Also for an assigned constant θ^*,

$$Cyc\,[\theta^*] \equiv \{f \in Cyc : f(\theta) = 0 \quad \text{for all } \theta < \overline{\theta}, \quad \text{for some } \overline{\theta} > \theta^*\},$$

$$\mathscr{F}\,[\theta^*] \equiv \{f \in \mathrm{R}^{(0,\infty)} : f(\theta) = \alpha h(\theta - \theta_0), \quad \text{for some } \alpha > 0 \quad \text{and} \quad \theta_0 > \theta^*\}.$$

We can now state (K_s):

(K_s). For each $\theta^* > 0$ and $f \in \mathscr{F}[\theta^*]$, there is a $\delta > 0$ (δ depending on f and θ^*) such that no accumulation function $C(\cdot)$ in $Cyc\,[\theta^*]$ satisfies

$$|C(\theta) - f(\theta)| < \delta\,, \qquad \text{for all } \theta.$$

Although the statement of (K_s) seems complicated, it has more or less the same meaning and implication as (K). Suppose we accept Serrin's interpretation of " Kelvin's law ", i.e., (K) is equivalent to that statement. If (K_s)

(7) *Cyc* is non-empty because we assume the existence of an ideal gas with constant specific heats. In fact we presume that there is quite a wide variety of cyclic thermodynamic processes.

is not true, then given any tolerance limit within which the net heat exchange between a body and its environment could be taken as negligible, we can always find an engine, working in cycles, which acts *practically* (i.e., after ignoring a negligible amount of net heat exchange) as a " perpetual engine of the second kind ". Thus (K_s) retains to some degree the flavor and the intuitive appeal of (K). (8)

§ 3. To prepare for the proof of the equivalence theorem, in this section we shall introduce some more notation and recall several facts concerning bodies of ideal gas with constant specific heats.

Suppose there is a body $\mathscr{B}_I$ of ideal gas with constant specific heats, and suppose we can have as many duplicates of $\mathscr{B}_I$ as we wish. Hereinafter we shall refer to the foregoing as " the assumption that there is an ideal gas with constant specific heats ".

By an equilibrium process that $\mathscr{B}_I$ may undergo we shall mean a process in which the temperature θ and the volume V of $\mathscr{B}_I$ are kept constant; by a Carnot process and a reversed Carnot process that $\mathscr{B}_I$ may undergo we shall mean any process in the duration of which the state of $\mathscr{B}_I$ traverses a Carnot cycle and a reversed Carnot cycle, respectively. These three kinds of cyclic processes constitute the class of C-processes that $\mathscr{B}_I$ may undergo. (9)

Let $I_C \subset R^{(0,\infty)}$ be defined by the property that $g \in I_C$ if and only if g is the accumulation function of some C-process that the body $\mathscr{B}_I$ may undergo. The following properties of I_C follow immediately from the definitions (ideal gas, Carnot cycles and reversed Carnot cycles, etc.), and the Laplace-Poisson law of adiabatic change for a body of ideal gas with constant specific heats (cf. Truesdell and Bharatha [10]):

(1) The zero function $0 \in I_C$.

(2) Every non-trivial (10) function $g \in I_C$ is defined in either one of the following two ways by three positive numbers C^+, θ^+, θ^- (with $\theta^- < \theta^+$), which denote the heat absorbed and the operating temperatures, respectively:

$$(i) \quad g(\theta) = C^+ h(\theta - \theta^+) - C^- h(\theta - \theta^-),$$

or

$$(ii) \quad g(\theta) = -(C^+ h(\theta - \theta^+) - C^- h(\theta - \theta^-)),$$

(8) The vagueness of " Kelvin's law " makes questionable any precise statement designed to express its meaning. Cf. Man [3] for more discussion on (K) and (K_s).

(9) Here we basically follow the definitions and terminology of Truesdell and Bharatha [10] except that we include equilibrium processes in the class of C-processes that $\mathscr{B}_I$ may undergo.

(10) A function in $R^{(0,\infty)}$ is said to be non-trivial if and only if it is not identically equal to the zero function.

where $C^- = \theta^- C^+/\theta^+$; conversely, given *any* three positive numbers C^+, θ^+, θ^- with $\theta^- < \theta^+$, (*i*) and (*ii*) above define, respectively, a non-trivial accumulation function in I_C.

(3) If $g \in I_C$, $-g \in I_C$.

(4) For any non-trivial $g \in I_C$, and any θ_a, θ_b $(\theta_a < \theta^- < \theta^+ < \theta_b)$,

$$\int_{\theta_a}^{\theta_b} \theta^{-1}\, dg = 0 .$$

The preceding integral is equal to zero for any θ_a, θ_b $(\theta_a < \theta_b)$ if g is the zero function.

(5) Given any $g \in I_C$ and any number $d > 0$, there is a C–process P of duration d, open to the body $\mathscr{B}_I$, with accumulation function $C_P(\cdot) = g$.

(6) $I_C \subset Cyc$.

§ 4. One further proposition essential to our proof is the following:

(*) $\quad f \in Cyc \quad$ and $\quad g \in I_C \quad$ implies $\; f + g \in Cyc$.

Here I sketch a plausible argument in support of (*): Suppose $f \in Cyc$ and $g \in I_C$. Then there is a body $\mathscr{B}$ and a cyclic process P_1 open to $\mathscr{B}$ such that $C_{P_1}(\cdot) = f$. Let d be the duration of P_1. By property (5) in § 3, $g \in I_C$ implies that there is a C–process P_2 open to the body $\mathscr{B}_I$ or its duplicate, of the same duration d and with accumulation function $C_{P_2}(\cdot) = g$. Using devices such as "adiabatic walls", etc., we let $\mathscr{B}$ and $\mathscr{B}_I$ *independently* execute the process P_1 and the process P_2, respectively, in the same interval of time $[0, d]$. Then the union system (i.e., the body which is the disjoint union of $\mathscr{B}$ and $\mathscr{B}_I$) executes a cyclic process in $[0, d]$ with an accumulation function $f + g$. Thus $f + g \in Cyc$.

The above argument can be formalized by using Serrin's "union axiom". However, if the reader is not convinced by the above argument, I advise him to take (*) as a *postulate*.

§ 5. In this paper by a (right-continuous) step function we shall mean the restriction to $(0, \infty)$ of a finite sum of functions which are real multiples of the right-translates of the Heaviside function $h(x)$, i.e., f is a step function if and only if $f = \alpha_1 h(\theta - \theta_1) + \cdots + \alpha_k h(\theta - \theta_k)$ for some $\theta_i > 0$, some real number α_i $(i = 1, \cdots, k)$ and some positive integer k. By properties (1) and (2) in § 3, every function in I_C is a step function. For an assigned positive constant θ^* we set $I_C[\theta^*] \equiv \{g \in I_C : g(\theta) = 0 \text{ for all } \theta < \overline{\theta}, \text{ for some } \overline{\theta} > \theta^*\}$.

The following lemma on step functions is essential to our proof of Lemma 2, which in turn will play a crucial role in our proof of the main theorem below.

LEMMA 1. *Let* $f:(0,\infty)\to \mathrm{R}$ *be a right-continuous step function,* $|f|<\mathrm{K}$. *If* f *is non-trivial, let* $\theta_0>0$ *be some number such that* $\theta_0<\inf\{\theta\in(0,\infty): f(\theta)\neq 0\}$. *Let* θ^* *be some number in* $(0,\theta_0)$. *Then* f *can be expressed as* $f=\alpha h(\theta-\theta_0)+g$, *where* α *is a constant,* $|\alpha|<\mathrm{K}$, *and* g *is a finite sum of functions in* $\mathrm{I_C}[\theta^*]$. *The above representation is also valid for* $f=0$ *by taking* $\alpha=0$ *and* $g=0$, *for any* $\theta_0>0$ *and* $\mathrm{K}>0$.

Proof. It suffices to consider non-trivial f because the assertion is obvious if $f=0$. Let $\theta_1,\theta_2,\cdots,\theta_k$ be the points of discontinuity of f, with $\theta_1<\theta_2<\cdots<\theta_k$. First suppose $k>1$. We shall add to f a function in $\mathrm{I_C}[\theta^*]$ such that the resultant function has fewer points of discontinuity than f.

For definiteness, suppose $f(\theta_{k-1})>f(\theta_k)$. Then let g_1 be the function defined by

$$g_1(\theta)=[f(\theta_{k-1})-f(\theta_k)]\,h(\theta-\theta_k)-(\theta_{k-1}/\theta_k)\,[f(\theta_{k-1})-f(\theta_k)]\,h(\theta-\theta_{k-1}).$$

Thus $g_1\in \mathrm{I_C}[\theta^*]$. Since

$$\begin{aligned} f(\theta_{k-1})+(-\theta_{k-1}/\theta_k)\,[f(\theta_{k-1})-f(\theta_k)] &= \\ =f(\theta_k)+[1-(\theta_{k-1}/\theta_k)]\,[f(\theta_{k-1})-f(\theta_k)]&, \end{aligned}$$

we conclude that $f+g_1$ is a right-continuous step function with its number of points of discontinuity $\leq k-1$, and $|f+g_1|<\mathrm{K}$. It is obvious that we can do the same trick if $f(\theta_{k-1})<f(\theta_k)$.

After we have repeated the same procedure m times, with $m\leq k$, each time adding to f a suitably chosen $g_i\in \mathrm{I_C}[\theta^*]$ $(i=1,2,\cdots,m)$, we can produce a function $f+g_1+g_2+\cdots+g_m$, which is a right-continuous step function, equal to zero for $\theta<\theta_0$, and has at most one point of discontinuity at θ_0; moreover, $|f+g_1+\cdots+g_m|<\mathrm{K}$. It follows immediately that $f+g_1+\cdots+g_m=\alpha h(\theta-\theta_0)$, for some constant α with absolute value $|\alpha|<\mathrm{K}$. Since $g_i\in \mathrm{I_C}[\theta^*]$ implies $-g_i\in \mathrm{I_C}[\theta^*]$, we finish the proof of the lemma for $k>1$ by taking $g=(-g_1)+\cdots+(-g_m)$. Similarly we can prove that the lemma is true for $k=1$. ///

Remark 1. Let g be the function as defined in Lemma 1. It is apparent from the above proof and property (4) in § 3 that if θ^* and θ_b are two temperatures such that (θ^*,θ_b) contains all the points of discontinuity of g, then

$$\int_{\theta^*}^{\theta_b}\theta^{-1}\,dg=0.$$

LEMMA 2. *Let* $\mathrm{C_P}(\cdot)$ *be the accumulation function of some process* P. *Let* $\theta^*>0$ *be some number such that* $\theta^*<\theta^{\mathrm{P}}_{\min}$. *Then there is a real number* α_0, *a positive real* $\theta_0>\theta^*$ *and a sequence of functions* $\{g_n\}$, *each* g_n *being a finite sum of functions in* $\mathrm{I_C}[\theta^*]$, *such that the sequence* $\{\alpha_0 h(\theta-\theta_0)+g_n\}$ *converges uniformly to* $\mathrm{C_P}(\cdot)$ *as* $n\to\infty$.

Proof. By hypothesis $C_P(\cdot)$ is a right-continuous function of bounded variation; thus $C_P = s + F$, where s is the right-continuous jump function associated with C_P, and $F = C_P - s$ is continuous. Let θ_a, θ_b be numbers such that $\theta^* < \theta_a < \theta^P_{\min}$ and $\theta_b > \theta^P_{\max}$. Then $s = F = 0$ for all $\theta < \theta_a$, and $s = \text{const.}$, $F = \text{const.}$ for all $\theta \geq \theta_b$. It follows from the properties of the jump function s and the continuous function F that we can find a sequence $\{f_n\}$ of right-continuous step functions that approaches C_P uniformly on $(0, \infty)$, $|f_n| < K$ for some constant K independent of n, and each f_n having all its points of discontinuity within the closed interval $[\theta_a, \theta_b]$. Let θ_0 be a point in (θ^*, θ_a).

By Lemma 1 each f_n, being a step function, can be decomposed as $f_n = \alpha_n h(\theta - \theta_0) + \bar{g}_n$, with $\bar{g}_n$ a finite sum of functions in $I_C[\theta^*]$, $|\alpha_n| < K$. Since $\{\alpha_n\}$ is a bounded sequence, we can find a convergent subsequence $\{\alpha_{n_k}\}$. Let $\alpha_0 = \lim_{n_k \to \infty} \alpha_{n_k}$. Then the sequence $\{\alpha_{n_k} h(\theta - \theta_0)\}$ converges to $\alpha_0 h(\theta - \theta_0)$ uniformly. It follows that the sequence $\{\bar{g}_{n_k}\}$ converges to $C_P - \alpha_0 h(\theta - \theta_0)$ uniformly, and the sequence $\{\alpha_0 h(\theta - \theta_0) + \bar{g}_{n_k}\}$ converges to C_P uniformly. We finish the proof by taking the sequence $\{\bar{g}_{n_k}\}$ as $\{g_n\}$. ///

We are now ready to prove the main theorem.

THEOREM 1. *If there is an ideal gas with constant specific heats,* (K_s) *and* (C—S) *are equivalent.*

Proof. (*i*) (K_s) implies (C—S).

Let $C_P(\cdot)$ be the accumulation function of some cyclic process P, and let θ^*, θ_b be numbers such that $\theta^* \in (0, \theta^P_{\min})$ and $\theta_b > \theta^P_{\max}$. Let $\{\alpha_0 h(\theta - \theta_0) + g_n\}$ be a sequence having the properties given in Lemma 2. We consider the sequence $\{C_P - g_n\}$. For each n, $C_P - g_n \in Cyc[\theta^*]$ by the proposition (*) in § 4. Since the sequence $\{C_P - g_n\}$ converges to $\alpha_0 h(\theta - \theta_0)$ uniformly and $\theta_0 > \theta^*$, we conclude that $\alpha_0 \leq 0$, for otherwise (K_s) will be violated. Thus we conclude from Helly's theorem and Remark 1 above that

$$\int_0^\infty \frac{1}{\theta}\, dC_P = \int_{\theta^*}^{\theta_b} \frac{1}{\theta}\, dC_P = \lim_{n\to\infty} \int_{\theta^*}^{\theta_b} \frac{1}{\theta}\, d\left(\alpha_0 h(\theta - \theta_0) + g_n\right)$$

$$= \frac{\alpha_0}{\theta_0} + \lim_{n\to\infty} \int_{\theta^*}^{\theta_b} \frac{1}{\theta}\, dg_n = \frac{\alpha_0}{\theta_0} \leq 0. \quad ///$$

(*ii*) (C—S) implies (K_s).

Let $\theta^* > 0$ and $f = \alpha h(\theta - \theta_0) \in \mathscr{F}[\theta^*]$ be given. Let δ be a number such that $0 < \delta < \alpha\theta^*/\theta_0$. Let $C_P(\cdot)$ be the accumulation function of some process P such that $\theta^P_{\min} > \theta^*$, and $|C_P(\theta) - f(\theta)| < \delta$ for all θ. Then

$C_P(\theta) \geq f(\theta) - \delta h(\theta - \theta^*)$ for all θ. By footnote (3) in § 1,

$$\int_0^\infty \frac{1}{\theta}\, dC_P = \int_0^\infty \frac{C_P}{\theta^2}\, d\theta \geq \int_0^\infty \frac{f - \delta h(\theta - \theta^*)}{\theta^2}\, d\theta = \frac{\alpha}{\theta_0} - \frac{\delta}{\theta^*} > 0 .$$

It follows from (C—S) that P cannot be cyclic, so $C_P(\cdot)$ is not in $Cyc\,[\theta^*]$. ///

§ 6. In this section we adopt option (II.) of footnote (2). Consider a body $\mathscr{B}$ with state space $\Sigma_{\mathscr{B}}$. Let P and $\overline{P}$ be processes open to $\mathscr{B}$ such that P ends and $\overline{P}$ starts at the same state. Then the process "P followed by $\overline{P}$", which we denote by $\overline{P} * P$, is defined and is open to $\mathscr{B}$. Moreover it is easy to see that

$$\int_0^\infty \frac{1}{\theta}\, dC_{\overline{P} * P} = \int_0^\infty \frac{1}{\theta}\, dC_{\overline{P}} + \int_0^\infty \frac{1}{\theta}\, dC_P .$$

If $\Sigma_{\mathscr{B}}$ and the processes open to $\mathscr{B}$ form a "system with perfect accessibility" (i.e., for any two states in $\Sigma_{\mathscr{B}}$ there is a process open to $\mathscr{B}$ which starts from one and ends at the other), for two fixed states σ_0, σ in $\Sigma_{\mathscr{B}}$ the set $a\{\sigma_0 \to \sigma\} \equiv \left\{ \int_0^\infty \theta^{-1}\, dC_P : \text{P starts from } \sigma_0 \text{ and ends at } \sigma \right\}$ is bounded above. It follows immediately that for a fixed σ_0 the "upper potential" $H(\sigma) \equiv \sup a\{\sigma_0 \to \sigma\}$ is a function of state and satisfies the inequality

$$(\#) \qquad H(\sigma_2) - H(\sigma_1) \geq \int_0^\infty \frac{1}{\theta}\, dC_P ,$$

for any process P that starts from σ_1 and ends at σ_2.[11] In the context of standard continuum thermodynamics, if we express the integrated Clausius-Duhem-Truesdell-Toupin inequality[12] for the pair ($\mathscr{B}$, P) in the form with the change in entropy standing on the left of the sign $\geq$ while all other terms

(11) The two preceding assertions are based in part on the first of the Bateman lectures which Owen gave at The Johns Hopkins University in October, 1979. (C—S) is employed in the proof of the first assertion.

(12) What we call here "the Clausius-Duhem-Truesdell-Toupin inequality" is usually called "the Clausius-Duhem inequality". It will do historical justice, however, to call that inequality (C—D—T—T) and to reserve the name "Clausius-Duhem inequality" for its special instance when the heat supply $r = 0$, because the term corresponding to that supply was introduced by Truesdell and Toupin ([11], Eq. (258.3)). We should blame neither Clausius nor Duhem if anything goes wrong because of the disputed term which involves r.

stand on the right, then the right-hand side of the integrated (C—D—T—T) inequality is identically equal to $\int_0^\infty \theta^{-1}\, dC_P$.(13) Thus the inequality (#) is simply the integrated (C—D—T—T) inequality for the pair ($\mathscr{B}$, P), if the upper potential H is taken as an entropy function.(14) That the strengthened "Kelvin's law" (K_s), for systems with perfect accessibility, should lead to the integrated (C—D—T—T) inequality raises a problem for those who reject (C—D—T—T) as being too severe a restriction. For further discussion on (C—D—T—T) and its foundations the reader may consult Man [3].

For bodies of a material with fading memory, (K_s) and (C—S) may lead to almost nothing because cyclic processes are so scarce. This fact raises the question of extending (K_s) and (C—S) so as to refer also to almost cyclic processes. That question is studied by Man [4].

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(13) I first learned of this identity in Serrin's Muncie lectures. There he stated the identity with $\int_0^\infty \theta^{-1}\, dC_P$ replaced by $\int_0^\infty \theta^{-2}\, C_P(\theta)\, d\theta$, and commented that the proof is "straightforward". For a detailed demonstration the reader may consult Man [3], Lemma 4.1.

(14) In stating the integrated (C—D—T—T) inequality for the pair ($\mathscr{B}$, P) we need only suppose that an entropy function be defined on $\Sigma_{\mathscr{B}}$; we need not assume that an entropy density exists.

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(Note added in proof. After this paper was submitted, I received from Professor Owen a manuscript by Coleman, Owen and Serrin, entitled "The Second Law of thermodynamics for systems with approximate cycles". In the covering letter Professor Owen wrote, "I enclose an unedited final draft of my joint paper with Coleman and Serrin containing new Accumulation Theorems for systems with approximate cycles. The proof of Accumulation Theorem (I), Section 5, is an adaptation of my proof of Serrin's Accumulation Theorem; the lemma I used in the latter proof appears as Lemma 3.2 in the enclosed manuscript ... [T]he present manuscript ... will be submitted for publication in the *Archive* [*for Rational Mechanics and Analysis*] as soon as some final editing for style is completed." While the memoir of Coleman, Owen and Serrin certainly has bearing on the question raised at the end of this paper, the above quotation provides us information on Owen's proof of Serrin's accumulation theorem, mentioned in footnote (5) above.)