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Proof that my work estimate implies the Clausius-Planck inequality

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Fisica matematica (Termodinamica). — *Proof that my work estimate implies the Clausius-Planck inequality.* Nota (*) del Socio straniero CLIFFORD TRUESDELL.

RIASSUNTO. — Ammessa la Prima Legge della Termodinamica, si prova la validità della Seconda Legge (Clausius–Planck) come conseguenza di una limitazione superiore per il rendimento di una macchina termica (anche irreversible), pubblicata dall'A. nel 1973.

1. BACKGROUND

Some years ago I showed [1] that the First Law of Thermodynamics,

$$L + \Delta E = C\,, \tag{I}$$

and the integrated Clausius-Planck Inequality,

$$\Delta H \geqq \int_{t_1}^{t_2} \frac{Q}{\theta}\, dt\,, \tag{C–P}$$

implied a general estimate for the work done:

$$L + \Delta E \leqq \left(1 - \frac{\theta_{\min}}{\theta_{\max}}\right) C^+ + \theta_{\min}\, \Delta H\,. \tag{W_0}$$

The notations are explained as follows:

L = work done by the body in question plus kinetic energy gained by it in the interval of time $[t_1\,, t_2]$,

$C\ := \int_{t_1}^{t_2} Q dt = C^+ - C^-$,

C^+ = heat absorbed by the body in $[t_1\,, t_2]$

$:= \frac{1}{2}\int_{t_1}^{t_2} (|Q| + Q)\, dt$,

C^- = heat emitted by the body in $[t_1\,, t_2]$

$:= \frac{1}{2}\int_{t_1}^{t_2} (|Q| - Q)\, dt$,

(*) Presentata nella seduta dell'8 marzo 1980.

E = internal energy of the body,

Δf: = increment of f in a specified closed interval,

Q = heating of the body,

θ = absolute temperature of the body,

H = entropy of the body,

θ_{min}, θ_{max} : = minimum and maximum values of θ during the closed interval to which L, ΔE, ΔH, C^+, and C^- refer.

The quantities L, E, Q, θ, and H are functions of time only, Thus the formulation is appropriate to the thermodynamics of homogeneous processes, in which all parts of a body have a common temperature at any one time. Q is assumed to be bounded and continuous except at a finite number of points, so it is integrable in the sense of Euler and Cauchy; θ is positive and continuous.

Fosdick and Serrin [2] later considered the effect of replacing (C–P) as an axiom by the Clausius-Duhem inequality for a single body subject to a non-uniform field of temperature. They supposed that body to be in contact with a reservoir at uniform but possibly time-dependent temperature τ, and they related the temperature at points in the body or on its surface to the bath temperature τ through Maxwell's heat-transfer inequalities. They concluded that

$$(W_{H-B}) \qquad L + \Delta E \leqq \left(1 - \frac{\tau_{min}}{\tau_{max}}\right) C^+ + \tau_{min} \Delta H .$$

Fosdick and Serrin noted also that the full strength of the First Law was not necessary for the proofs of these work estimates: The weaker inequality

$$(I^-) \qquad L + \Delta E \leqq C$$

would do just as well as (I).

Still later, Muncaster and I noticed [3] that Fosdick and Serrin's assumptions sufficed for the truth of the *heat-bath inequality*:

$$(H—B) \qquad \Delta H \geqq \int_{t_1}^{t_2} \frac{Q}{\tau} \, dt .$$

This inequality has just the same form as (C—P), but it differs in meaning, for $\tau(t)$ is the temperature of the surroundings of the body at the time t, and nothing need be assumed directly about the temperature field within and upon the surface of the body to which L, Q, ΔE, and ΔH refer.

It is plain that if (W_0) is replaced by (W_{H-B}) while (C—P) is replaced by (H—B), the difference is one of notation alone. Therefore, if (I^-) and (C—P) $\Rightarrow (W_0)$, then also (I^-) and (H—B) $\Rightarrow (W_{H-B})$. Thus to derive their result (W_{H-B}), which refers to no temperatures other than those of the surroundings of the body with which L, ΔE, C^+, and ΔH are associated, Fosdick and Serrin need not have appealed to the Clausius-Duhem inequality and to Maxwell's heat transfer inequalities. To obtain their results, the heat-bath inequality (H—B) suffices.

2. PROGRAM

My purpose here is to prove a converse to my theorem on the maximum work done in a homogeneous process and at the same time a converse to Fosdick and Serrin's extension of it to a body in a heat bath. Only the formal structure provided by (I) and (W_0) is needed. In fact it suffices to replace (I) by a weaker statement which is the opposite of (I^-):

$$(I^+) \qquad L + \Delta E \geqq C .$$

Subject to specified assumptions of smoothness, I shall establish the schema

$$(I^+) \text{ and } (W_0) \Rightarrow (C\text{—}P) .$$

The schema previously established is

$$(I^-) \text{ and } (C\text{—}P) \Rightarrow (W_0) .$$

From the two together we conclude the schema

$$(I) \text{ and } (W_0) \Longleftrightarrow (I) \text{ and } (C\text{—}P) .$$

The same reasoning applies when (W_0) is replaced by (W_{H-B}). Therefore, both for a body in which the field of temperature is constant at each time and for a body immersed in a heat bath we may replace the usual " Second Law " by a mathematically equivalent assumption about *the maximum possible work done by an assigned amount of heat absorbed, in association with assigned increments of energy and entropy.*

We shall now render the new schema precise. To make the reasoning clearer we shall at first replace θ_{min} and θ_{max} by virtually arbitrary positive functions a and b defined on the set of closed subintervals of $[t_1, t_2]$.

3. THE MAIN INEQUALITY AND ITS MAIN CONSEQUENCE

We begin from a general inequality which subsumes (W_0) and (W_{H-B}):

$$(W_{gen}) \qquad L + \Delta E \leqq \left(1 - \frac{a}{b}\right) C^+ + a\Delta H .$$

Combining this inequality with (I^+) yields

$$\Delta H \geqq \frac{1}{a}\left[C - \left(1 - \frac{a}{b}\right) C^+\right] = \frac{C^+}{b} - \frac{C^-}{a} .$$

The quantities a and b here are positive constants associated with the interval to which the symbol Δ refers, say $[t_0 - h, t_0 + h]$. Then

$$\frac{C^+}{b} - \frac{C^-}{a} = \frac{1}{2b} \int_{t_0-h}^{t_0+h} (Q + |Q|)\, dt + \frac{1}{2a} \int_{t_0-h}^{t_0+h} (Q - |Q|)\, dt =$$

$$= \frac{1}{2}\left(\frac{1}{a} + \frac{1}{b}\right) \int_{t_0-h}^{t_0+h} Q dt - \frac{1}{2}\left(\frac{1}{a} - \frac{1}{b}\right) \int_{t_0-h}^{t_0+h} |Q|\, dt .$$

We fix t_0; then a and b become functions of h alone. We assume that Q is continuous on $[t_0 - h, t_0 + h]$, so we may use the mean-value theorem to express the integrals above in terms of numbers ξ and η in the interval $[-h, h]$:

$$\frac{1}{2h}\left(\frac{C^+}{b} - \frac{C^-}{a}\right) = \frac{1}{2}\left(\frac{1}{a} + \frac{1}{b}\right) Q(t_0 + \xi) - \frac{1}{2}\left(\frac{1}{a} - \frac{1}{b}\right) |Q(t_0 + \eta)| .$$

Thus the above inequality for ΔH can be written as

$$\frac{\Delta H}{2h} \geqq \frac{1}{2}\left(\frac{1}{a} + \frac{1}{b}\right) Q(t_0 + \xi) - \frac{1}{2}\left(\frac{1}{a} - \frac{1}{b}\right) |Q(t_0 + \eta)| .$$

This *main inequality* allows several deductions. For most of these we consider a positive, continuous function Θ on the interval $[t_0 - h, t_0 + h]$, and we take a and b as Θ_{min} and Θ_{max}. Then (W_{gen}) becomes my original work inequality (W_0) if $\Theta = \theta$, Fosdick and Serrin's generalization if $\Theta = \tau$. With Θ uncommitted we obtain from the main inequality its *main consequence*:

$$\frac{\Delta H}{2h} \geqq \frac{1}{2}\left(\frac{1}{\Theta_{min}} + \frac{1}{\Theta_{max}}\right) Q(t_0 + \xi) - \frac{1}{2}\left(\frac{1}{\Theta_{min}} - \frac{1}{\Theta_{max}}\right) |Q(t_0 + \eta)| .$$

4. The theorem and other consequences

Since Θ is a continuous function on $[t_0 - h, t_0 + h]$, there are numbers δ and ε in $[-h, h]$ such that

$$\Theta_{min} = \Theta(t_0 + \varepsilon) , \; \Theta_{max} = \Theta(t_0 + \delta) .$$

Then the main consequence takes the form

$$\Delta H \geqq h \left(\frac{1}{\Theta(t_0 + \varepsilon)} + \frac{1}{\Theta(t_0 + \delta)}\right) Q(t_0 + \xi)$$

$$- h \left(\frac{1}{\Theta(t_0 + \varepsilon)} - \frac{1}{\Theta(t_0 + \delta)}\right) |Q(t_0 + \eta)| .$$

Now we suppose that Q is continuous on some closed interval. We partition that interval into n equal subintervals and apply the foregoing inequality to each. We sum these n inequalities, let n tend to ∞, appeal to the definition and existence theorem for the Euler-Cauchy integral of a continuous function, and so establish (C—P). Finally we consider a Q which is bounded and has only finitely many discontinuities. Then we may write (C—P) for each subinterval on which Q is continuous. Summing the finite sequence of inequalities so obtained, we demonstrate the following

THEOREM. *Let* L , Q , E, *and* Θ *be functions of time on the interval* $[t_1, t_2]$; *let* Θ *be positive and continuous*; *let* Q *be integrable in the Euler-Cauchy sense*; *and suppose that on all closed subintervals of* $[t_1, t_2]$

$$(\mathrm{I}^+) \qquad L + \Delta E \geqq C,$$

and

$$L + \Delta E \leqq \left(1 - \frac{\Theta_{\min}}{\Theta_{\max}}\right) C^+ + \Theta_{\min} \Delta H .$$

Then

$$(\mathrm{C—P}) \qquad \Delta H \geqq \int_{t_1}^{t_2} \frac{Q}{\Theta}\, dt .$$

Of course $\Delta H = H(t_2) - H(t_1)$, while C, C^+, and C^- are determined from Q by the definitions given in § 1. This theorem establishes the first schema stated in § 2 and hence also the equivalence stated there.

Assumptions partly weaker and partly stronger suffice to draw another conclusion from the main inequality. Namely, if we consider a time t_0 at which H is differentiable, then we need only assume that a and b are continuous functions of h at $h = 0$ to conclude that

$$\dot{H} \geqq \frac{1}{2}\left(\frac{1}{b(0)} + \frac{1}{a(0)}\right) Q - \frac{1}{2}\left(\frac{1}{a(0)} - \frac{1}{b(0)}\right) |Q|,$$

$$= \begin{cases} \dfrac{Q}{b(0)} & \text{if } Q \geqq 0, \\[2ex] \dfrac{Q}{a(0)} & \text{if } Q \leqq 0. \end{cases}$$

This inequality is to be interpreted in terms of the generalized work estimate (W_{gen}). The choice $a = \Theta_{\min}$, $b = \Theta_{\max}$ reduces the new inequality to identity with the former one at times when H is differentiable: $\Theta \dot{H} \geqq Q$.

The main consequence in § 3 allows us to infer also a coarse lower bound for ΔH in a closed interval of time during which Q is continuous, namely

$$\frac{\Delta H}{\Delta t} \geqq \frac{1}{2}\left(\frac{1}{\Theta_{\min}} + \frac{1}{\Theta_{\max}}\right) Q_{\min} - \frac{1}{2}\left(\frac{1}{\Theta_{\min}} - \frac{1}{\Theta_{\max}}\right) |Q|_{\max} .$$

5. Comments on teaching

I think the equivalence stated in § 2 provides a way to introduce the Second Law for possibly irreversible processes that beginners in engineering may find more suggestive than the traditional mysticism about entropy. The teacher may tell his students something along these lines: We have proved the existence of internal energy E and entropy H for bodies susceptible only of reversible processes. For general processes, possibly irreversible, we shall assume that the quantities E and H as functions of time still exist and satisfy *the same basic relations*:

1) Heat, work, and internal energy remain universally and uniformly interconvertible.

2) The effects of irreversibility *do not increase* the maximum amount of work a body can do in a process for which $\theta_{\max}$, $\theta_{\min}$ (or $\tau_{\max}$, $\tau_{\min}$), C^+, ΔE and ΔH are prescribed.

Then we can derive the traditional "Second Laws" (C—P) and (H—B) as proved theorems.

I have used the Euler-Cauchy integral because with it the proof is not only rigorous but also accessible to students of engineering at the very beginning of their study of the calculus. Moreover, I do not see that greater generality would serve any purpose in the applications for which classical thermodynamics is intended or that lesser generality would suffice to justify them.

6. Comments on the results

A–*Corners*. The usual Clausius-Planck inequality is obtained by differentiating (C—P) : $\theta \dot{H} \geqq Q$. At the corners of a Carnot cycle in classical thermodynamics H exists, but $\dot{H}$ and Q generally do not exist. Thus the differentiated inequality makes no sense at corners. The results given above, on the contrary, take care of difficulties of this kind. They apply easily to classical thermodynamics and to the theory of bodies with linear friction [4].

B–*History*. Clausius [5] obtained something like (C—P) but without reference to the time and with use of an undefined and unexplained integration $\int \cdots dC$. He arrived at his inequality through a process of divination which suggested to him that an amount of heat C gained from a reservoir at the temperature θ provided an "equivalence value" C/θ which served as a lower bound for ΔH, and that in an adiabatic change H could not increase. In symbols,

$$\Delta H \geqq \frac{C}{\theta} \quad \text{if } \theta \text{ remains constant in the interval to which C and } \Delta H \text{ refer,}$$

$$\Delta H \geqq 0 \quad \text{if } Q = 0 \text{ in that interval.}$$

Adding inequalities of this kind shows that if a body gains amounts of heat $C_1, C_2, \cdots, C_n$ from n reservoirs at temperatures $\theta_1, \theta_2, \cdots, \theta_n$ and is otherwise calorically insulated, then

$$\Delta H \geqq \sum_{k=1}^{n} \frac{C_k}{\theta_k} .$$

Hence, claimed Clausius, $\Delta H \geqq \int dC/\theta$ in general. (C—P) interprets Clausius' unexplained integration $\int \cdots dC$ as being $\int_{t_1}^{t_2} \cdots Q\, dt$. Conversely, all the finite inequalities asserted by Clausius are immediate consequences of (C—P).

My treatment has points of similarity with Clausius', but the differences are more important:

a) My basis is not physical divination but an explicit assumption about maximum possible work. (Thus my approach is in Carnot's spirit.)

b) My analysis proceeds through mathematical statements and mathematical proofs.

c) My result applies to a body immersed in a heat bath, whether or not the temperature be the same at all points of the body.

The point where my posture is most likely to be criticized, however, is one it has in common with Clausius': Both assume *a priori* that an entropy function defined at all times in some interval is associated with the body in question, and neither specifies constitutive relations by which that function may be determined.

Perhaps it is worth remarking that two of the results here, namely the main consequence in § 3 and the coarse lower bound at the end of § 4, do not require the function H to exist except at the beginning and the end of the interval of time over which Q and H are defined. Thus they cannot be liturgically set aside by those who reject the concept of entropy except for processes which begin and end in some special circumstances.

C–*The two weakened First Laws.* Let us return for a moment to the weakened First Laws which appear in the schemata written in § 1:

$$(\mathrm{I}^-) \qquad L + \Delta E \leqq C ,$$

$$(\mathrm{I}^+) \qquad L + \Delta E \geqq C .$$

We may interpret (I^-) as saying that if we put heat into a body we cannot get in return for it more than an equal amount of work and energy. Some heat may simply disappear. The second schema states that the Clausius-Planck inequality then delivers the same upper bound for $L + \Delta E$ as we get in the theory of reversible processes. Some disappearance of heat, then, will certainly not give us *more* work and energy than a reversible Carnot cycle would produce. We may interpret (I^+) as saying that when a body does work and gains energy, it cannot gain an amount of heat greater than the sum of those. Some work and energy may simply disappear. The first schema states that the upper bound for $L + \Delta E$ according to the thermodynamics of reversible processes implies (C—P). Even the disappearance of some work and energy, provided that irreversibility do not increase the total quantity $L + \Delta E$, does not *lessen* the classical minimum increase of entropy.

The above remarks should not be read as claims that the First Law itself should be weakened in one or the other sense of inequality. We may interpret the first schema as telling us that if irreversibility leaves unaffected the upper bound for $L + \Delta E$, then our own possible failure to account for the entire work done and energy gained will not impair the classical lower bound for ΔH. We may interpret the second schema as asserting that if we adopt the classical lower bound for ΔH, then failure on our part to account for all the heat taken on by a body will not enable us to get any more work and energy from the heat we know we did put into the body. When expressed in this way, the first two schemata become obvious to anyone who knows the third schema.

D–*Uniqueness*. While in the classical thermodynamics of reversible processes the entropy of a body is unique to within an additive constant, in more general recent theories there is no reason to expect any such uniqueness. For most purposes of application any function having the properties we associate with entropy is sufficient; it is neither necessary nor desirable that that function be unique. The theorems established in this note are invariant under replacement of the function H by any function H^* such that $\Delta H^* \geqq \Delta H$.

Acknowledgment. Mr. Serrin's comments on the first draught of this note enabled me to strengthen my results, in particular to replace (I) by (I^+) and to conclude (C—P) directly from the main inequality without assuming H to be differentiable. I thank also Messrs. Fosdick, C.–S. Man, and Owen for their comments and suggestions. The work presented here was supported in part by a grant from the programs in Applied Mathematics and Solid Mechanics of the U.S. National Science Foundation.

References

[1] C. TRUESDELL (1973) – *The efficiency of a homogeneous heat engine*, « Journal of Mathematical and Physical Sciences » (Madras) 7, 349–371, and 9 (1975), 193–194; *Sul rendimento delle macchine termiche omogenee*, « Accad. Naz. dei Lincei, Rend. Cl. Sci. Fis. Mat. », (8) *53* (1972), 550–553 (1973); *Improved estimates of the efficiencies of irreversible heat engines*, « Annali di Mat. Pura ed Applic. » (4) *108* (1976), 305–323.

[2] R. L. FOSDICK and J. SERRIN (1975) – *Global properties of continuum thermodynamic processes*, « Arch. Rational Mech. Anal. », 59, 97–109.

[3] C. TRUESDELL and R. G. MUNCASTER (1980) – *Fundamentals of Maxwell's Kinetic Theory of a Simple Monatomic Gas, treated as a Branch of Rational Mechanics*, New York etc., Academic Press. See Section (v) of Chapter I, where we prove the statement in the text above under the assumption that there are no sources of heat but without requiring the field τ to be constant at each time. If τ is a function of time alone, it is easy to include sources of heat.

[4] These bodies seem to have been introduced into thermodynamics in a wasted lecture, « Thermodynamics for beginners », pp. 373–389 of « Proc. IUTAM Symposia Vienna 1966 »; Wien and New York, Springer, 1968. An improved treatment may be found in Chapter I of my *Rational Thermodynamics, A Course of Lectures on Selected Topics*, New York etc., McGraw-Hill, 1969, and further results in my paper in the *Annali di Matematica*, cited in reference 1.

[5] For an account of Clausius' work see § 11D of my *Tragicomical History of Thermodynamics, 1822–1854*, New York, Springer-Verlag, 1980.