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MANUEL MONLÉON PRADAS
JOSÉ LUIS GOMEZ RIBELLES

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Poincaré's Proof of Clausius' Inequality

Manuel Monléon Pradas
José Luis Gomez Ribelles
Universidad Politecnica de Valencia - Spain
Dept. de Termodinamica Aplicada

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Abstract. Clausius's inequality occupies a central place among thermodynamical results, as the analytical equivalent of the Second Law. Nevertheless, its proof and interpretation have always been debated. Poincaré developed an original attempt both at interpreting and proving the result. Even if his attempt cannot be regarded as succeeded, he opened the way to the later development of continuum thermodynamics.

Résumé. L'inégalité de Clausius joue un rôle central dans la thermodynamique, comme résultat analytiquement équivalent au Deuxième Principe. Mais son interprétation et sa démonstration ont toujours fait l'objet de débats. Poincaré a saisi les deux problèmes, en leur donnant des vues originales. Même si on ne peut pas dire que son essai était complètement réussi, il a ouvert la voie aux développements ultérieurs de la thermodynamique des milieux continus.

1. Debates over Clausius' Inequality

The statements of the Second Law of thermodynamics due to Carnot, Clausius, Kelvin and Planck are qualitative assertions about restricted classes of processes: they all refer to cycles, some refer to reversible cycles (Carnot, Kelvin in 1854), others do to cycles exchanging heat at two temperatures (Carnot, Clausius), still others to cycles exchanging heat at a single temperature (Kelvin in 1851) or to cycles not emitting any of the absorbed heat (Kelvin in 1851, Planck). The plausibility of this axiom, founded on its proximity to experience, excludes at this level statements involving wider classes of processes. But this immediately arose the question whether there was some *universal* consequence of the law, extending beyond the set of processes touched by it. This is the role played since by Clausius' inequality in thermodynamics.

In his 1854 memoir [Clausius 1854] R. E. Clausius introduced what he called the "equivalence-value" of an elementary 'transformation': the quotient of the heat dQ and a function of empirical temperature that he immediately identified as the temperature measured on the gas scale (the perfect gas temperature scale), T. In terms of this 'equivalence-value' dQ/T he 'proved' what he and later authors were to regard as the "analytical expression of the Second Law" [Clausius 1864, 147] (a law he himself had stated in 1850 [Clausius 1850], freeing 'Carnot's principle' from caloric adherences): in reversible cycles "the algebraical sum of the [equivalence-value of the] transformations must be zero" [Clausius 1864, 145],

$$\oint \frac{dQ}{T} = 0. \qquad (1)$$

In words (but not in *formulae*!) Clausius then stated that for *any* (not necessarily reversible) cycle "the algebraical sum of all transformations can only be negative" [Clausius 1864, 152]:

$$\oint \frac{dQ}{T} \leq 0 . \tag{2}$$

This is the celebrated *Clausius inequality*. If his reasoning leading to it is followed [Clausius 1864, 133-145] it becomes clear that in (2) the symbol T stands for the temperature *of the environment* of the system under study, *i.e.*, the temperature of those bodies which exchange heat with the one under consideration. But two years later in [Clausius 1856], Clausius again states the result (2) — now, for the first time, as a formula — and regards T as the temperature *of the system* undergoing the process:

> T is a function of the temperature of the changing body in that moment in which it takes in the element of heat dQ, or, if the body has different temperatures in its different parts, of the temperature of that part of it which takes in dQ. [Clausius 1864, 161]

Weak as the proofs of (1, 2) under the first interpretation of T were, for this second interpretation Clausius offered no proof at all! A period of fertile application and development of the consequences of the newly established 'mechanical theory of heat' followed after these first steps, and the successes of the theory focused all attention; the weak foundation on which some of its results stood seemed not to bother researchers and users. Some of them explicitly adhered to one or the other interpretation of the results, others proposed their own; still others simply ignored the issue [see Monléon 1997].

But during the 1880's the problems were suddenly realized by a number of authors. In [Clausius 1854] Clausius had considered the proof of (2) to be contained in that of (1), and this last was valid only for bodies undergoing homogeneous processes. How could one apply the same ideas to arbitrary cycles? J. Bertrand was one of the first to point out explicitly to this difficulty:

> If all the points of the body under study have not retained during the transformation a common value of temperature, what becomes of the ratio dQ/T of the quantity of heat given to the body, at temperature T, and of the integral of this ratio? Is it necessary to decompose the body into infinitely small elements and reunite the integrals extended over each of them? The proof of the theorems does not allow it. [Bertrand 1887, 266]

The influential Gabriel Lippmann raised further criticisms on Clausius' arguments. He considered that

> the inequality [(2)] is a consequence of the equality [(1)]; it doesn't

> teach us anything new, let alone express, as somebody might have thought, some truth applicable only to non-reversible cycles. [Lippmann 1889, 229];

he even finished his treatise on thermodynamics with the surprising assertion:

> Thus, it cannot be affirmed that, in all cases, and without restriction, $\int dQ/T \leq 0$. [Lippmann 1889, 232]

Another frenchman, Pierre Duhem, soon to become an illustrious thermodynamicist, had seen his first submitted Ph. D. Thesis rejected by the same G. Lippmann on grounds of his interpretation and use of Clausius' inequality:

> In this very extense study Mr. Duhem intends to treat several physical and chemical phenomena with the aid of a thermodynamical principle which he attributes to Mr. Clausius, and which supposedly would be as follows: for all closed cycles the integral: $\int dq/T$ has always a negative value; dq denoting the infinitesimal quantity of heat developed at temperature T. This formula: $\int dq/T<0$ is indeed found in Clausius; but with a different meaning, and accompanied by commentaries and essential restrictions which seem to have escaped the author. As a consequence, this result cannot be attributed to Clausius as conceived by the author.[1]

Thus stood the panorama at the time Poincaré lectured on thermodynamics, in 1888-1889. Besides his own, significant contributions to clarify the matter were going to come from Carl Neumann [1891] in 1891 and from Max Planck [1897] in 1897. However, controversy over the meaning, scope and proof of (2) has never faded since those times, and has arrived to our days in almost the same terms cast by the authors mentioned in the above paragraphs (see [Monléon 1997] for an extense study and pertinent references).

In the present work we analyze Poincaré's interpretation and proof of the Clausius inequality. We disentangle its steps in the next section. In the subsequent section we scrutinize the *nucleus* of the proof, where, at the same time, lie the most original (unprecedented and never again followed) suggestions of Poincaré. A critical assessment is finally presented in the last section.

2. Poincaré's Proof

Two different problems must be confronted when faced with

1 From the report of the commission appointed to judge the thesis; quoted in [Brouzeng 1987, 31-33].

the expression (2) of Clausius' inequality: *what is the meaning* of the terms under the integral sign and of the integral itself (does T refer to the temperature of the system experiencing a transformation, or does it refer to that of its environment? how is the integral to be defined if the process is not homogeneous)? and: *how can the inequality be proved* (under the interpretation chosen) starting from the second law.

Poincaré adhered to Clausius' 1856 interpretation of (2) — see our quote of Clausius in the introduction — but endorsed Bertrand's criticism as to the absence of a satisfactory proof of it. In a sense, his (a mathematician's) task he saw as one of logical hygiene, not as an assessment of the degree of *truth* of the result itself:

"I am not going to probe into its generality [...]; only the experimenter is called to settle these questions", [Poincaré 1892, xv] (in what follows we always quote from this work). He thus set himself the task of "fixing the precise meaning of the inequality" and "of searching the hypothesis to be associated with Clausius' axiom in order that the inequality follows with necessity from it". [*ibid.*, xv]. In this endeavour he was prepared to transit the way suggested by Bertrand:

> The gravest [of the objections raised] is that relative to the temperature, for, if the temperature of the system is not uniform, the integral of Clausius has not anymore a precise meaning [...] It is nevertheless possible to give a demonstration of Clausius' theorem immune to those objections. [...] In the first place it will be necessary to define well what is to be understood by $\int dQ/T$. [212]

Here his proposal:

> We can thus represent Clausius' integral by
>
> $$\iint \frac{dQ}{T}$$
>
> thus indicating that two integrations are needed, one extended over the cycle elements of each elementary system [into which the total system is divided], the other extended to all elements of the total system. [214]

This seems to mean: if the system S performs a cycle in time interval $[t_1,t_2]$ then so does each one of its volume elements $dV(x)$ (where x is the location of $dV(x)$); integrate then dQ/T over $t \in [t_1,t_2]$ at constant x, and then integrate the result over $x \in$ S. Obviously this requires to consider temperature as place and time dependent, $T = T(x,t)$. *Poincaré felt the need to translate the up to then dominant finitistic tradition of thermodynamics into a continuum theory* employing field concepts.

How could such a complicated idea be proved from the startlingly simple formulations accepted (then and now) for the second law of thermodynamics?

The route chosen was certainly tortuous. It starts in #107 and ends in #188 of [Poincaré 1892], extending over more than a hundred pages. The result itself, together with all its preliminaries, thus occupies a central part of Poincaré's treatise. Five steps can be distinguished in his proof.

1. In ##107-111 Poincaré considers uniform homogeneous systems whose states can be described by the independent variables *(v,p)*, specific volume and pressure ('Clapeyron's representation') and whose isotherms and adiabats are well-behaved, in the sense that the two families have the usual properties of decussating precisely once and spanning the whole range of temperatures (*ideal* systems).

2. For this class of systems he considers in #120 *reversible, homogeneous* cycles and proves the equality (1) for them [p. 139-141]. Here *T* is the temperature measured on the scale defined in the classical way exploiting the consequences of the second law for the efficiency of Carnot cycles [p. 138].

3. The result of #120 relied on the properties of adiabats and isotherms of *ideal* systems, and on the second law. In #150 Poincaré notices that not all systems can be supposed to behave in this way: water in the vicinity of 4 degrees Celsius (the anomaly of density) violates this behaviour. In this paragraph [pp.182-186] Poincaré extends (1) to reversible, homogeneous cycles of these *(v,p)*-uniform, but *anomalous*, systems. (His argument cannot be taken as a proof. Moreover, though he believes that he needs this result, step 4 of his proof relies only on the properties of the non-anomalous systems of steps 1 and 2.)

4. With this result at hand he proves in ##175-182 Clausius' inequality (2) for all *cycles in which T is uniform.* Systems can now be arbitrary, and cycles need not be reversible, although they still need proceed with the system's temperature uniform at each instant. This step is the central one in Poincaré's proof (we devote the next section to a detailed analysis of it and of the next one). With the help of the properties of ideal systems (steps 1 and 2 above) and an argument employing a *composite system* he proves what we call (in order to stress its role) "Poincaré's lemma" [p. 214]. With it, he proceeds to prove a result he attributes to Potier & Pellat [p. 218], namely, that in all cycles (we must add: in which a system exchanges the heat quantities Q_i with a finite number of constant-temperature heat *foci* at, respectively, the absolute temperatures Θ_i)

$$\sum_i \frac{Q_i}{\Theta_i} \leq 0 . \tag{3}$$

From this result Poincaré claims to conclude that

$$\oint \frac{dQ}{\Theta} \leq 0 \tag{4}$$

when the environment of the system consists not in a finite number of constant-temperature bodies, but in (one or more) bodies with a continuous distribution of temperature. Notice that, at this stage of the proof, the difference between (4) and Clausius' inequality (2) lies in that, first, the system undergoes a cycle with uniform temperature, and, second, that dQ is divided through the environment's temperature in (4) and through the system's temperature in (2). Finally, Poincaré proves that in (4) the temperature Θ can be replaced by the system's (uniform) temperature T, thus getting the result stated at the beginning of this paragraph.

5. The proof comes to its end in ##183-185 [pp. 223-227]. Here Poincaré not only proves that

$$\iint \frac{dQ}{T} \leq 0 \tag{5}$$

(the *double integral*, as said, extends over place and time, (x,t); T is the temperature of the system at (x,t), and Q is the time rate at which heat is exchanged at time t by the volume element at place x *with its exterior*), but also that

$$\iint \frac{dQ_e}{T} \leq 0 . \tag{6}$$

Here Q_e means the time rate of heat exchange of a volume element of system S with the exterior of S (and not with its own exterior, as in (5)). It is properly (6) what can be paired to Clausius' inequality (2), as Q in this last is always meant to be the heat exchange of a system with its environment. In passing from (5) to (6) Poincaré assumes a certain heat transfer hypothesis and proves, as an intermediate step, what we call "Poincaré's inequality",

$$\iint dq\left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0 , \tag{7}$$

an example of a *heat transfer inequality*.

(For the sake of completeness we point out that, in a now standard way, the *entropy inequality* $\Delta S \geq \iint dQ/T$ is obtained in #188, p. 231.)

This is the sketch of Poincaré's proof of Clausius' inequality. Of course, he does not identify its steps in the way we have done; this the reader must provide himself. He even is not clear at all in what must be considered his central thesis, namely his interpretation of Clausius' integral as a double integral: only in words — and without symbols like *(x,t)*, which we have added as a help in rendering his interpretation — does Poincaré describe what kind of operation is intended in (5,6).

Two ideas seem original in Poincaré's development: his transfer of the result to the continuous medium (steps 4 and 5), and his explicit notice of the need of auxiliary (we called them *ideal*) systems in the proof of a result intended for arbitrary, general systems (steps 1 and 2). *The proof of Clausius' inequality requires a family of systems endowed with special constitutive properties.* Up to its first occurrences in [Poincaré 1892] and [Neumann 1891] this issue had passed unnoticed in the literature. It remained obscure and unrecognized for many years, until recent literature has underlined the need of so called "thermometric assumptions", or "thermometric substances". Poincaré himself reluctantly acknowledged in the preface to [Poincaré 1892]:

> [I] have given two proofs of Clausius' theorem: the first one valid only for certain classes of systems, the second one completely general, but resting on the first one. It turns out that I could not avoid making an artificial distinction between two kinds of bodies, according to whether their states can or cannot be defined by two variables only. This distinction, which doesn't correspond to anything in actuality, does show up once and again in this work. I had to attach to it an enormous importance, although nothing was more strange to my own thoughts. [Poincaré 1892, xiv-xv]

The fact that the assumption of certain constitutive properties of *special* systems has consequences for all remaining systems and processes is a point of central importance in thermodynamics, and is based upon the use of some notion of *system composition*. Though already employed by Carnot, Kelvin and Clausius, it was always informally. Poincaré is here no exception. We undertake a reconstruction of steps 4 and 5 of the proof in our next section (we there employ our own notations to clarify and lay bare Poincaré's procedure as well as his hidden assumptions).

3. Analysis

The equality (1), proved for reversible cycles of *(v, p)*-homogeneous systems, leads immediately — in a now standard way — to the definition of an *entropy* function for this class of systems. In what we have called step 4 of his proof Poincaré considers a thermally isolated process $\bar{p}$ of a system C, the system C itself being composed by n systems "of the type considered up to now", $A_1, ..., A_n$, "so that each one of them possesses an entropy" [214], and m other arbitrary systems, $B_1, ..., B_m$, "of indeterminate nature, so that one cannot speak of their entropies".

The process $\bar{p}$ is such that, besides being adiabatic, the subsystems B_k must all perform a cycle in it. Thus, they can exchange heat only among themselves and with the A_j's. Poincaré considers the *composite system*

$$C = A_1 \otimes ... \otimes, A_n \otimes B_1 \otimes ... \otimes B_m,$$

and the process $\bar{p}$ of C, the 'composite process' arising from the processes a_j of A_j and b_k of B_k, $\bar{p} = a_1 \otimes ... \otimes, a_n \otimes b_1 \otimes ... \otimes b_m$. If $\Delta S(a_j)$ denotes the change of the entropy of system A_j in process a_j, Poincaré proves what we single out as his fundamental lemma,

> *Poincaré's lemma*: If $\bar{p} = a_1 \otimes ... \otimes b_m$ is a process of C such that (a) b_k is a cycle of B_k, (b) the a_j start and end in homogeneous states, and (c) $\bar{p}$ is adiabatic, then $\sum_{j=1}^{n} \Delta S(a_j) \geq 0$.

This result reappears in [Planck 1897], with the same pivotal role. The proof Poincaré gives of this lemma rests on (i) the properties of the well-behaved adiabats and isotherms of the *ideal systems* A, (ii) on Kelvin's 1851 version of the second law, and (iii) on (tacit) *modal assumptions*: he considers it as *possible* that, after the completion of $\bar{p}$, C returns to its initial state in a process r in which the B's remain isolated from the A's, and these exchange heat with a common constant-temperature heat reservoir (the resulting cycle $\bar{p}r$ of C is then a monothermal process, of the type restricted by Kelvin's version of the second law; see [Monléon 1997] for a complete discussion):

> Our cycle consists of two parts [...] At the end of the first part the systems B have returned to their initial states, not so the systems A. In the second part of the cycle the systems B suffer no alteration. In the first part of the cycle the system C is thermally isolated [...] The heat exchanged thus reduces to the heat taken in from the exterior in the second part of the cycle. But this heat has been taken from a single source. Consequently, according to one of the statements of Carnot's theorem, no production of exterior work can take place. [217]

Poincaré then considers a cycle of an arbitrary system S which exchanges the heats Q_i with bodies at temperatures Θ_i. He invokes the *possibility* of "considering the sources of heat as being of the same nature as the systems A of the previous lemma" ([p. 218]; again a *modal hypothesis*!); as these have entropies and they are easily determined, he immediately obtains (3). After writing down this result (p. 218), he says:

> This inequality can be written as
>
> $$\int \frac{dQ}{\Theta} \leq 0,$$
>
> with dQ representing the amount of heat given to the system by one of the sources during an elementary transformation, and Θ being the temperature of this source. [*ibid.*]

Poincaré has skipped in this way the difficulties linked with the passage to the continuous case. Obviously, this is no proof at all, not even in an informal sense. Even if similar reasonings are met still today in many textbooks and papers, the reader must be aware that this is merely *hocus pocus*. Recall that the proof of Potier & Pellat's (3) linked every Q_i with a body in the environment of the system S, and that all of them were *composed* into a single system for the proof to work. A passage 'to the continuous case', were it to proceed along the lines suggested by Poincaré (and by so many later authors), would thus previously require a meaningful notion of composition for a non-countable infinity of systems!

Poincaré then turns to systems in processes with uniform temperature: "Let us consider a system in which the temperature is not uniform and, moreover, varies with time. In a given instant [t] the temperatures of all points are comprised between two temperatures [$T_u(t) > T_l(t)$], themselves varying with time" [219]; if $dQ^+(t)$ is the heat absorbed by the system from some sources and $dQ^-(t)$ is the heat emitted to some other sources by the system "during the infinitely small time interval following this time instant" t, then he claims that

$$\int \frac{dQ^+(t)}{T_u(t)} - \int \frac{dQ^-(t)}{T_l(t)} \leq 0 \qquad \text{in all cycles.}$$

To see it, "[l]et us suppose that we have n sources of heat, $\alpha_1, \ldots, \alpha_n$, whose temperatures $\Theta_1, \ldots, \Theta_n$ stand in increasing arithmetic progression of ratio ε" [220] and are such that $\Theta_i > T_u(t) > \Theta_{i-1}$ and $\Theta_k < T_u(t) < \Theta_{k+1}$. "The amount of heat $dQ^+(t)$ [...] *can be supposed* originating in the source α_i, whose temperature is greater than that of any of the points of the system at the instant considered. Analogously, *it can be admitted* that $dQ^-(t)$ is emitted by the system to the source α_k, whose temperature is less than that of any of the points of the system" ([220]; we have emphasized the assumptions of a *modal* character being made by Poincaré). If now

> dQ_m denotes the heat taken in from the source α_m,
>
> $$\sum \frac{dQ_m}{\Theta_m} = \frac{dQ^+}{\Theta_i} - \frac{dQ^-}{\Theta_k} > \frac{dQ^+}{T_u - \varepsilon} - \frac{dQ^-}{T_l - \varepsilon} .$$
>
> Integrating over the complete cycle,
>
> $$\sum \frac{Q_i}{\Theta_i} > \int \frac{dQ^+}{T_u + \varepsilon} - \int \frac{dQ^-}{T_l + \varepsilon} .$$
>
> But $\Sigma Q_i/\Theta_i \leq 0$ by the theorem of Potier & Pellat, what proves that
>
> $$\int \frac{dQ^+}{T_u + \varepsilon} - \int \frac{dQ^-}{T_l + \varepsilon} < 0 ;$$
>
> ε being arbitrary, this proves the result. [221]

If the system has uniform temperature at each time then $T_u(t) = T_l(t)$, and the result is proved.

This completes step 4 of the proof. Poincaré gathers what he considers to have been the sole hypothesis of his argument:

> Notice that only two hypothesis were employed for the demonstration of this result: 1) the temperature of *any point* given in the system is perfectly determinate at *each instant*; 2) if a phenomenon takes place absorbing heat from certain sources, its realization is equally *possible* if the supply of heat stems from an arbitrary source subject to the only condition that its temperature be greater than that of any of the points of the system. [222]

We have placed emphasis in the quotation on two items. First, it is clear that Poincaré understands *temperature* to be a meaningful concept in non-homogeneous (and thus, non-equilibrium) circumstances of systems: 'temperature' must be specified as a field of temperatures, $T = T(x, t)$. Second, modalities are being made use of in the argument. We have repeatedly pointed out the places where *possibility* of certain events (distinct from those taking place actually) is being invoked. Should one try to formalize this, something like what follows would be needed:

Let $r = p \otimes e$ be a process, where p is the process of a system S and e is the (actual) process of its environment during p. Then there is another process $r^* = p^* \otimes e^*$ of the system and its environment such that $p = p^*$ and e^* satisfies [...]

Here [...] stands for the list of conditions to be invoked of e*. (Of course, nothing of the like is present in [Poincaré 1892]. It is only recently that a reflection on hidden modal assumptions in physical theories has begun, see [Bressan 1981].)

Once he has proved Clausius' inequality for cycles with uniform-temperature Poincaré sees a straightforward way to its generalization to *continua*:

> When the temperature of the system is not uniform, this system is to be decomposed into an infinity of infinitely small systems, each one of them with uniform temperature. When the total system executes a cycle, each one of the small systems performs accordingly a cycle. Thus, for any one of the elementary systems $\int dQ/T \leq 0$, and for the total system $\iint dQ/T \leq 0$, the second integration extending over all elements of the system. [224]

(Here again Poincaré's reasoning is informal, not a proof strictly. A physicist would not know how to interpret or compute the result; a mathematician, in addition, wouldn't know how to follow the lead.)

Still this is not the Clausius inequality.

> [I]n this integral dQ represents the amount of heat that one of the elementary systems takes in from the exterior as well as from the rest of the elementary systems composing the total system. Let us put $dQ = dQ_e + dQ_i$, with dQ_e denoting the heat absorbed by the system originating in the exterior of the total system and dQ_i denoting that which results from the interior exchanges. We shall have
>
> $$\iint \frac{dQ}{T} = \iint \frac{dQ_e}{T} + \iint \frac{dQ_i}{T} \leq 0 .$$
>
> Consequently, if we prove that $\iint dQ_i/T$ is positive, $\iint dQ_e/T \leq 0$ will have been demonstrated. To prove this point, let us consider two elementary systems with uniform temperatures T_1 and T_2, with $T_1 > T_2$. The first system will give out to the second system the amount of heat dq. These systems contribute to the integral the difference
>
> $$-\frac{dq}{T_1} + \frac{dq}{T_2} = dq\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
>
> which is necessarily positive [...]. The same happens for all exchanges of heat among the elementary systems, so
>
> $$\iint \frac{dQ_i}{T} = \iint dq\left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0$$
>
> and thus
>
> $$\iint \frac{dQ_e}{T} \leq 0 .$$
>
> [225-226]

This inequality is meant to be the content of Clausius' inequality, and the proof is complete.

We point out here that the inequality (7), which we call 'Poincaré's inequality', is a general result, valid for all processes, even if it appears in the course of an argument intended for cycles (this inequality, or rather the expression Poincaré gives for it, suffers from the same ambiguities of interpretation as do (5) or (6)).

We have quoted Poincaré at length in this step. Even if his purpose is clear and his line of argument can be understood, what he writes is not a proof of what he claims. And perhaps even worse, he leaves essential ambiguities in his expressions, as he is not formal enough in the introduction of the field concepts: he does not display the arguments of the functions being integrated, nor the domains of integration. (That this is not a 'formal' criticism may be seen in the fact that two different interpretations can be given of Poincaré's 'double integral', $\iint dQ/T$: if the 'second integration' must extend over the complete system S, then the 'first integration' itself must deliver some kind of set function, say μ, whose value on S would be $\iint dQ/T$:

$$\mu(S) = \int_s d\mu = \iint \frac{dQ}{T}$$

As is usual in continuum theories, let the heat exchanged by any subbody $\Delta \subset S$ be expressed as

$$\int_{t_1}^{t_2} \left(\int_\Delta r dV + \int_{\partial\Delta} s dA\right) dt$$

with r body heating, $s = \vec{h} \cdot \vec{v}$ surface heating, and $\partial\Delta$ the boundary of Δ. The volume-density of the heating is $r + div\,\vec{h}$, but what is the volume-density of μ? Is it $\int[(r + div\,\vec{h})/T]dt$, in which case

$$\iint \frac{dQ}{T} = \int_s \int_{t_1}^{t_2} \frac{r + div\vec{h}}{T} dt dV,$$

or is it $\int [(r / T) + div(\vec{h}/T)]dt$, in which case

$$\iint \frac{dQ}{T} = \int_s \int_{t_1}^{t_2} \frac{r}{T} dt dV + \int_{\partial s} \int_{t_1}^{t_2} \frac{S}{T} dt dA\ ?$$

Both interpretations can in fact be met in the literature. The second one leads to the so called *Clausius-Duhem inequality*.

> In one of his very ingenious prefaces Mr. Bertrand mocks with great finesse all those authors who in their works pile up harsh integrals which they would never know how to calculate [...] In this chapter [on the Clausius' inequality] I, more than anyone else, deserve this criticism, and I would have no excuse weren't it for my purpose of promoting the understanding of the inequality [...]. [Poincaré 1892]

4. Balance

In his *Thermodynamique*, H. Poincaré has developed an original attempt both at *interpreting* Clausius' integral and at *proving* Clausius' inequality under that interpretation. Both the interpretation of Clausius' integral *and* the proof of Clausius' inequality ("the analytical equivalent of the second law of thermodynamics", as it was then often called) had always been controverted (this is true still today!). Among his achievements is the explicit notice of the need to consider a certain class of distinguished *special* systems *composed* with the general type of system object of study (though incomplete, his treatment of 'anomalous systems' is also one of the first and few ever).

Poincaré thought that the scope of the result required the framework of field concepts. Although Clausius' integral itself had already been interpreted by Kelvin [*in* Thomson 1882] in terms of continuum concepts, Poincaré's is maybe the first attempt (and one of the few ever tried) of a proof of Clausius' inequality in such a theoretical setting. Though his notations were never free of ambiguity (his self-criticism on p. xvi, quoted above, is revealing), use of place and time dependent fields is clearly implied as the tool to solve the difficulty represented by arbitrary, non-homogeneous processes. This was really a novelty, which departed from the already classical line of the known proofs (which originated in Kelvin's 1854 paper). These last seemed to be inextricably tied to the consideration of processes with only a *finite* number of heat exchange temperatures (since only a composition of a finite number of systems does make sense), and thus were unsuited for more general situations. Some really new idea had to be expected from Poincaré's thesis. He did not succeed in this respect. The original way in which he casts his final result (his 'double integral') cannot obscure the fact that he retains the *nucleus* of the traditional proof (the essential step constituted by the result attributed by Poincaré to Potier & Pellat), and that the passage to the continuum limit can then only be invoked or suggested, but not proved (even after an overwhelming use of what we have identified as — explicit as well as hidden — modal assumptions).

Poincaré recognized and seized a problem, and increased the plausibility of one of the interpretations of Clausius' inequality, that which makes use of the temperature of the system as a meaningful field concept in arbitrary, non-equilibrium processes. His (along with Kelvin's and Duhem's) is one of the precursors of the modern development of continuum thermodynamics.

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