We analyze some aspects of the third law of thermodynamics. We first review both the entropic version (N) and the unattainability version (U) and the relation occurring between them. Then, we heuristically interpret (N) as a continuity boundary condition for thermodynamics at the boundary $T = 0$ of the thermodynamic domain. On a rigorous mathematical footing, we discuss the third law both in Carathéodory’s approach and in Gibbs’ one. Carathéodory’s approach is fundamental in order to understand the nature of the surface $T = 0$. In fact, in this approach, under suitable mathematical conditions, $T = 0$ appears as a leaf of the foliation of the thermodynamic manifold associated with the non-singular integrable Pfaffian form $\delta Q_{rev}$. Being a leaf, it cannot intersect any other leaf $S = \text{const.}$ of the foliation. We show that (N) is equivalent to the requirement that $T = 0$ is a leaf. In Gibbs’ approach, the peculiar nature of $T = 0$ appears to be less evident because the existence of the entropy is a postulate; nevertheless, it is still possible to conclude that the lowest value of the entropy has to belong to the boundary of the convex set where the function is defined.

I. INTRODUCTION

We re-analyze the status of the third law of thermodynamics in the framework of a purely thermodynamic formalism. After a discussion of the status of the third law in current physical literature, and after an heuristic justification of the entropic version, we set up a rigorous mathematical apparatus in order to explore the actual necessity for a third law of thermodynamics. The approach by means of Pfaffian forms to thermodynamics, introduced by Carathéodory, is the most powerful tool for understanding the problems which can occur in thermodynamic formalism at $T = 0$. In our analysis of the latter topic the Pfaffian form $\delta Q_{rev}$ is expressed in terms of independent extensive variables. One finds that $T = 0$, as an integral manifold of $\delta Q_{rev}$, can be a leaf of the thermodynamic foliation if sufficient regularity conditions for the Pfaffian form are ensured. Contrarily, $T = 0$ is intersected by the (would-be) leaves $S = \text{const.}$ which occur at $T > 0$. The third law appear then as a condition which has to be imposed if a foliation of the whole thermodynamic manifold, including the adiabatic boundary $T = 0$, has to be obtained.

Also Gibbs’ approach is analyzed. Carathéodory’s and Gibbs’ approaches together allow to better define the problem of the third law.

The plan of the paper is the following. In sect. II and in sect. III a discussion of the third law and of its standard proofs is given. A particular attention is devoted to Landsberg’s studies, which are under many respects corner-stones on this topic. In sect. V we remark that Planck’s restatement of the third law is not conventional but mandatory for homogeneous systems. In sect. IV, we try to understand, from the physical point of view, if it is possible to give a purely thermodynamic justification for the third principle in the entropic version (N). We show that the third principle in the entropic version can be in a natural way interpreted as a continuity boundary condition, in the sense that it corresponds to the natural extension of thermodynamics to the states at $T = 0$. In sect. VI it is shown that, in the framework of Carathéodory approach, (N) is equivalent to ensuring that the surface $T = 0$ is a leaf of the thermodynamic foliation associated with the Pfaffian form $\delta Q_{rev}$. The isentropic surfaces cannot intersect the $T = 0$ surface, because no common point between distinct leaves of the foliation determined by $\delta Q_{rev}$ is allowed. Some problems arising when (N) is violated are discussed, and it is recalled that a singular behavior occur if the entropic version (N) fails. In sect. VII a Gibbsian approach to the problem is sketched. We show that the entropy can reach its minimum value (if any) only on the boundary $T = 0$ of its domain.
II. THE THIRD LAW

The third law of thermodynamics has been formulated in two ways. The original formulation of Nernst concerns the behavior of the entropy of every system as the absolute zero of the temperature is approached. Particularly, the entropic side of Nernst’s theorem (N) states that, for every system, if one considers the entropy as a function of the temperature \( T \) and of other macroscopic parameters \( x^1, \ldots, x^n \), the entropy difference \( \Delta S \equiv S(T, x^1, \ldots, x^n) - S(T, \bar{x}^1, \ldots, \bar{x}^n) \) goes to zero as \( T \to 0^+ \)

\[
\lim_{T \to 0^+} \Delta S = 0 \tag{1}
\]

for any choice of \( (x^1, \ldots, x^n) \) and of \( (\bar{x}^1, \ldots, \bar{x}^n) \). This means that the limit \( \lim_{T \to 0^+} S(T, x^1, \ldots, x^n) \) is a constant \( S_0 \) which does not depend on the macroscopic parameters \( x^1, \ldots, x^n \). Planck’s restatement of (N) is

\[
\lim_{T \to 0^+} S = 0 \tag{2}
\]

and it is trivially mandatory for homogeneous systems (cf. sect. V). The other formulation concerns the unattainability (U) of the absolute zero of the temperature. The (U) side can be expressed as the impossibility to reach the absolute zero of the temperature by means of a finite number of thermodynamic processes. Both the above formulations are due to Nernst, and they are equivalent under suitable hypotheses, as it has been remarked in Refs. [2–4] and e.g. also in Refs. [5,6].

The third law has a non definitively posed status in standard thermodynamics and a statistical mechanical basis for it is still missing. Counter-Examples to (2) have been constructed [7,8], whereas in Ref. [9] models displaying a violation of (1) are given. Moreover, the validity of thermodynamics for finite-size systems if \( T \) is sufficiently near the absolute zero has been questioned. A corner–stone of this topic is represented by Planck’s objection (see Ref. [10] and references therein) against a thermodynamic description of a “standard” system below a given temperature, due to a reduction of the effective degrees of freedom making impossible even to define an entropy. The same problem is analyzed in Ref. [11] where the breakdown of thermodynamics near the absolute zero is shown in the case of a Debye crystal. Thermodynamic formalism is shown to fail because of finite size effects. Indeed, if the finite size of a real thermodynamic system is taken into account, according to Ref. [11] near the absolute zero it is no more possible to neglect statistical fluctuations in the calculation of thermodynamic quantities like e.g. \( T, S \) because they are of the same order as the “standard” leading terms\(^1\). There is a relative uncertainty in the definition of equilibrium states which is of order one. Of course, if one considers for the number of degrees of freedom a mathematical limit to infinity, then the formal success of the thermodynamic approach follows. For more details see Ref. [11]. See also Ref. [12]. We don’t discuss this topic further on in this paper. In Refs. [11,13] it is proposed, in agreement also with the general axiomatic approach of Refs. [2,3], that the third law should be assumed as the position of a boundary condition for the thermodynamic differential equations, whose experimental validation is stated in regions above the absolute zero. Moreover, according to statements in Refs. [2,4], the thermodynamic variables on the “boundary set” of the states at absolute zero temperature could be conventionally defined as suitable limits (not depending on the path used to approach a particular state at \( T = 0 \)) of the thermodynamic variables in “inner points” of the thermodynamic configuration space and this is proposed as the only satisfactory approach to the definition of thermodynamic variables at the absolute zero [2,3]. To some extent, the application of the thermodynamic equations to the absolute zero should be considered as a rather formal extrapolation of the theory in a region beyond its confirmed domain of validity, and this could be considered as the main reason for introducing a new postulate beyond the zeroth, the first and the second law [13]. In sect. IV we come back on this topic and give an interpretation of Nernst Heat Theorem as a “continuity” boundary condition for thermodynamics at \( T = 0 \).

Concluding this section, it is also remarkable that the third principle, if considered as an impotence principle in analogy with the first and the second principle [14], in the (U) version simply does not allow to get \( T = 0 \), whereas in the (N) version implies also that the work produced by an arbitrarily efficient Carnot machine between \( T_2 > T_1 \) (that is, a thermal machine with efficiency arbitrarily near \( 1^- \)) vanishes as \( T_1 \to 0^+ \) (see Ref. [15]). For an extensive discussion upon the third law see also Refs. [16–18].

\(^1\)The example of Ref. [11] involves a Debye crystal having a volume \( V \sim 1\text{cm}^3, \langle N \rangle \sim 10^{21} \); statistical fluctuations are of the same order as the leading terms for \( T \sim 10^{-5}\text{K} \).
We start by discussing (U) and (N) in standard thermodynamics. The double implication (U)⇔(N), according to the analysis developed in Refs. [2,4], relies on some hypotheses that it is interesting to recall.

A. (U)⇔(N) in Landsberg’s analysis

A detailed analysis shows that in standard thermodynamics unattainability (U) implies (N) if the following conditions are satisfied [2,4]:

a) The stability condition \((\partial S/\partial T)_{x_1,\ldots,x_n} > 0\) is satisfied for any transformation such that the external parameters (or deformation coordinates) \(x_1,\ldots,x_n\) are kept fixed; these transformations be called isometric transformations [14].

This hypothesis is in general ensured by the suitable convexity/concavity properties of the thermodynamic potentials and is given for ensured in Landsberg’s works [2–4]. It is useful to explicit this hypothesis.

b) There are no multiple branches in thermodynamic configuration space.

For the condition b) an equivalent statement is “in thermodynamic space no boundary points different from the \(T = 0\) ones occur” [2], that is, no first-order phase transitions are allowed. In our setting, this requirement amounts to choosing a continuous entropy function.

c) There is no discontinuity in thermodynamic properties of the system near the absolute zero.

In Ref. [2] a careful discussion of the conditions to be satisfied in order to ensure (U) is contained. In particular, by following Ref. [2], if a),b),c) hold and moreover (N) fails, then \(T = 0\) is attainable. If a),b) and c) hold, then (U) implies (N). If a),b) hold and (N) fails, then (U) implies that a discontinuity near the absolute zero has to occur, and such a discontinuity has to prevent the attainability of \(T = 0\) (violation of c)) [2]. Landsberg makes the example of an abrupt divergence in the elastic constants of a solid as a conceivable ideal process preventing a solid violating (N) to reach a zero temperature state by means of quasi–static adiabatic volume variations (the hypothesis of Ref. [2] is compatible with the vanishing near \(T = 0\) of the (adiabatic) compressibilities that are related with elastic constants in ordinary thermodynamics; particularly, for standard systems one can define the compressibility modulus as the inverse of the compressibility; it is proportional to the Young modulus in the case of a solid). Anyway, in standard thermodynamics a violation of c) is ruled out and is not discussed further on in Ref. [2]. Moreover, in standard treatment of the third law (U) is associated with the impossibility to get states at \(T > 0\) isoentropic to states at \(T = 0\), so that c) is not taken into account. A further discussion is found in the following subsections.

FIG. 1. (a): Multi–branches structure of the thermodynamic space. According to Landsberg, it implies the validity of (U) and the violation of (N). (b): Violation of (N) that implies a violation of (U), due to the presence of the isoentropic AB. Landsberg conjectures that (U) holds if a discontinuity near \(T = 0\) occurs. See also the text. In (a) and (b) the dashed regions are forbidden.
In Refs. [2,4] a further condition “entropies don’t diverge as \( T \to 0^+ \)” takes into account the standard behavior of thermodynamic systems near the absolute zero. This condition is not necessary if one considers a non-negative concave entropy (cf. sect. VII). It can be relaxed when infinite values of the parameters are allowed [19]. E.g., in the non-standard case of black hole thermodynamics, the above condition is not necessary, and in Ref. [20] the divergence of the entropy occurring in the infinite mass limit for the black hole case is discussed.

Possible failures of the implication \((U) \Rightarrow (N)\) are discussed also in Ref. [5], both in the case of reversible processes and in the case of irreversible ones.

**B. \((N) \Rightarrow (U)\) in Landsberg’s analysis**

The isoentropic character of the zero temperature states is considered a condition ensuring the unattainability (see e.g. Ref. [13] and Refs. [2,3]). A full implication \((N) \Rightarrow (U)\) is possible in the case of thermodynamic processes which consist of an alternate sequence of quasi-static adiabatic transformations and quasi-static isothermal transformations \((\text{class } P(x) \text{ according to Refs. } [2,3])\). Actually, a more general notion of unattainability can be assumed: “zero temperature states don’t occur in the specification of attainable states of systems”. This is almost literally the \((U)\) principle as in Refs. [2,3]. \((U)\) states that no process allows to reach states at \( T = 0 \), even as transient non-equilibrium states. Then \((N)\) can fail and \((U)\) can still be valid: In general, the latter hypothesis allows a de-linking of \((U)\) and \((N)\) and implies that \((N) \neq (U)\) and \((U) \neq (N)\) \([2,3]\). But such a de-linking occurs under particular conditions: the failure of the implication \((U) \Rightarrow (N)\) requires again a rejection of one of the hypotheses \(b),c\) above, whereas \((N) \Rightarrow (U)\) fails if processes not belonging to the aforementioned class \(P(x)\) allow to reach \( T = 0\) \([2,3]\).

For the sake of completeness, we recall in the following subsection also the standard approach to Nernst’s theorem, which involves heat capacities \([13,18]\).

**C. \((U) \Leftrightarrow (N)\) by means of heat capacities: the standard proof**

The implication \((U) \Rightarrow (N)\) can be obtained also as follows. It implicitly requires that conditions \(a),b),c\) of Landsberg hold. Let us consider two states \((T_1, x^1 \ldots x^n), (T_2, y^1 \ldots y^n)\) and the related entropies

\[
S(T_1, x^1, \ldots, x^n) = S(0, x^1, \ldots, x^n) + \int_0^{T_1} \frac{dT}{T} C_{x^1,\ldots,x^n}(T)
\]

\[
S(T_2, y^1, \ldots, y^n) = S(0, y^1, \ldots, y^n) + \int_0^{T_2} \frac{dT}{T} C_{y^1,\ldots,y^n}(T)
\]

where \(S(0, x^1, \ldots, x^n), S(0, y^1, \ldots, y^n)\) are the limits of the above entropies as \( T \to 0^+ \); in the standard proof one assumes also that \((T_1, x^1 \ldots x^n), (T_2, y^1 \ldots y^n)\) lie on the same isoentropic surface and that it is possible to perform a quasi-static adiabatic process connecting them \([13,18]\). If \(T_2 = 0\), then one gets

\[
S(0, y^1, \ldots, y^n) - S(0, x^1, \ldots, x^n) = \int_0^{T_1} \frac{dT}{T} C_{x^1,\ldots,x^n}(T)
\]

and this implies that, if \(S(0, y^1, \ldots, y^n) - S(0, x^1, \ldots, x^n) > 0\) and the stability condition \(C_{x^1,\ldots,x^n}(T) > 0\) holds, a temperature \(T_1\) satisfying the last equation always exists, so the unattainability requires \(S(0, y^1, \ldots, y^n) - S(0, x^1, \ldots, x^n) \leq 0\). The same reasoning applied to the process \((T_2, y^1, \ldots, y^n) \to (0, x^1 \ldots x^n)\) gives the opposite inequality \(S(0, y^1, \ldots, y^n) - S(0, x^1, \ldots, x^n) \geq 0\) and so one has to conclude that \(S(0, y^1, \ldots, y^n) = S(0, x^1, \ldots, x^n)\) \([13,18]\). The convergence of the above integrals of course requires a suitable behavior for the heat capacities. It is remarkable that, according to this standard proof, \((U)\) is implemented by forbidding the presence on the same isoentropic surface of states at \( T = 0 \) and states at \( T > 0 \). Thus isoentropic transformations reaching \( T = 0 \) cannot exist. This is a key point. Indeed, one could also allow for a different implementation of \((U)\) in which formally states at \( T > 0 \) and states at \( T = 0 \) lie on the same isoentropic surface but, because of some hindrance arising in a neighborhood of \( T = 0 \), the isoentropic transformation reaching \( T = 0 \) actually cannot be performed. This is the reason for the hypothesis \(c)\) of Landsberg.

The converse, that is, the implication \((N) \Rightarrow (U)\), is based on the implicit assumption that processes, which don’t belong to class \(P(x)\) and which allow to reach \( T = 0 \), don’t exist \([2-4]\). It is straightforward \([18]\): Let us consider an adiabatic reversible process \((T_1, x^1 \ldots x^n) \to (T_2, y^1 \ldots y^n)\). If \((N)\) holds, then there is no possibility to reach a
Indeed, along an adiabatic transformation
\[
S(T_1, x^1, \ldots, x^n) = S(T_2, y^1, \ldots, y^n) \iff \int_{T_0}^{T_1} \frac{dT}{T} C_{x^1, \ldots, x^n}(T) = \int_{T_0}^{T_2} \frac{dT}{T} C_{y^1, \ldots, y^n}(T)
\]
and it is evident that, if the final state is \((T_2 = 0, y^1, \ldots, y^n)\), then
\[
\int_{T_0}^{T_1} \frac{dT}{T} C_{x^1, \ldots, x^n}(T) = 0,
\]
which is impossible for \(C_{x^1, \ldots, x^n} > 0\). The same conclusion holds if an adiabatic transformation from \((T_1, x^1, \ldots, x^n)\) to \((0, y^1, \ldots, y^n)\) is considered. This proof assumes that the only possibility to get \(T = 0\) is by means of a reversible adiabatic transformation. The latter is a reasonable hypothesis, because any thermal contact and any irreversibility cannot be successful in obtaining \(T = 0\) due to the second law. For an interesting proof of the above statements see also Ref. [21].

IV. NAIVE NERNST HEAT THEOREM: A CONTINUITY BOUNDARY CONDITION FOR THERMODYNAMICS AT \(T = 0\)

We assume here a physical attitude, and wonder if it is possible to give a purely thermodynamic justification for the third principle in the entropic version \((N)\). This section is dedicated only to an heuristic discussion. A rigorous mathematical setting for the third law is found in the following sections.

We stress that, in our reasoning herein, we adopt substantially Landsberg’s point of view as expressed e.g. in Ref. [4], p. 69: “... one must imagine one is approaching the physical situation at \(T = 0\) with an unprejudiced mind, ready to treat a process at \(T = 0\) like any process at \(T > 0\). With this attitude the maximum information concerning conditions at \(T = 0\) can be deduced...”

Let us assume that transformations along zero temperature states are allowed. In a reversible transformation at \(T > 0\) it is known that \((\delta Q)_\text{rev} = T \, dS\).

As a consequence,
\[
\Delta S = 0 \text{ for adiabatic reversible transformations at } T > 0.
\]

Then, let us consider ideally which behavior is natural to postulate for thermodynamics at \(T = 0\). Along the \(T = 0\) state by means of an adiabatic transformation. That is, if \((N)\) holds, then \((N)\) and the second law imply \((U)\).

The underlying hypotheses are:

\(\eta_0\) \(T = 0\) belongs to the equilibrium thermodynamic phase space;
\(\eta_1\) it is possible ideally to conceive transformations at \(T = 0\);
\(\eta_2\) transformations at \(T = 0\) are adiabatic reversible;
\(\eta_3\) transformations at \(T = 0\) are isoentropic;
\(\eta_4\) there is a continuous match between states at \(T = 0\) and states at \(T > 0\).

Actually, \(\eta_4\) could even summarize all the hypotheses above, in the sense that a violation of at least one hypothesis \(\eta_0, \eta_1, \eta_2\) and \(\eta_3\) would imply a discontinuity in thermodynamics between zero temperature states and non-zero ones. Concerning \(\eta_1\), we recall that Landsberg substantially rejects it, because he postulates a poor population of
zero temperature states in order to forbid the $T = 0$ transformation in the Carnot-Nernst cycle. Each state can be associated with its von Neumann entropy and a priori a violation of (N) and a discontinuity are allowed. There is in any case a postulate about the density of the zero temperature states which is “discontinuous” with respect to the assumptions for the states at $T > 0$.

The path of Nernst consists in starting from the violation of the Ostwald’s formulation of the second law which is implicit in a special Carnot cycle, which has the lower isotherm at $T = 0$. See the figure below. We refer to this cycle as the Carnot-Nernst cycle. If it were possible to perform it, it would imply the existence of a thermal machine with efficiency one, which is a violation of the second law of thermodynamics. Note that the violation of the identification between adiabats and isentropes is implicit in the $T = 0$ isotherm of the Carnot-Nernst cycle. In order to avoid this violation, Nernst postulates therefore the unattainability (U) of the absolute zero (see also Ref. [22]).

### A. Transformations at $T = 0$

Criticisms against this path, relating the third law to the second one have a long history (see Refs. [3,10,23,24,15,25] and references therein) which starts with Einstein’s objection. Einstein underlines that near $T = 0$ dissipations begin being non-negligible [23]. This would make the Carnot-Nernst cycle unrealizable because the adiabatic $T = 0$ could not be performed. This kind of criticism could be moved also against any attempt to define transformations at $T = 0$. Nevertheless, it is true that a postulate on thermodynamics is required at $T = 0$, as variously realized in literature (see e.g. Ref. [10]). The objection against the Carnot-Nernst cycle can also avoid referring to irreversibility arising near $T = 0$, as discussed e.g. in Refs. [24,25]. The point is that one reaches the $T = 0$ surface by means of an adiabatic reversible transformation, say BC, and that also any transformation CD at $T = 0$ has to be adiabatic (see the figure below).

![Figure 2. Carnot-Nernst cycle in the plane $T - S$.](image-url)

Then, it does not seem possible for the system to be carried along the CD transformation contained in the $T = 0$ surface [24,25] because the adiabatic constraint applies to BC as well as to CD and so an operative procedure (no matter how ideal) to carry on the cycle seems to be missing. It is to be noted that, by analogy with the operative definition of isothermal transformation at $T > 0$, from a physical point of view, the system should also be considered to be in thermal contact only with a “source at $T = 0$”. The non-sense, in the case of $T = 0$, is evident; a “source at $T = 0$” should be defined (a device able to exchange large (arbitrary) amounts of heat without changing its temperature). The point is that one reaches the $T = 0$ surface by means of an adiabatic reversible transformation, say BC, and that also any transformation CD at $T = 0$ has to be adiabatic (see the figure below).

This kind of reasoning implies a failure of the thermodynamic formalism at $T = 0$, because of the impossibility to give a satisfactory prescription for implementing transformations at $T = 0$. In particular, the problem is related with the existence of the intersection between adiabatic surfaces (any isentropic surface intersecting the $T = 0$ surface is an adiabatic surface which intersects the very peculiar adiabatic surface $T = 0$), because of the apparent absence of tools allowing to pass from one to another one adiabatically. In some sense, we find an incompleteness of the thermodynamic formalism at $T = 0$, because there are serious problems in defining an operative procedure [23–25]. Nevertheless, we wish to underline that, in line of principle, it could be still possible to implement the adiabatic transformation at $T = 0$ as a distinct adiabatic transformation, because, even if an adiabatic constraint is required,
The third law of thermodynamics (Planck restatement) corresponds to a regularity condition of the Pfaffian equation \( \delta Q_{\text{rev}} = 0 \) on the boundary \( T = 0 \) of the thermodynamic manifold. It is equivalent to the request that a well-defined foliation of the whole thermodynamic manifold exists.

In the following sections, we discuss the problem in a mathematically rigorous framework.

V. ABSOLUTE ENTROPY AND PLANCK’S POSTULATE

In our discussion of the third law, the zero-temperature entropy constant is undetermined, with the only constraint \( S_0 \geq 0 \) suggested by statistical mechanical considerations. Planck’s restatement of (N) requires \( S_0 = 0 \), that is, \( S \to 0^+ \) as \( T \to 0^+ \), because the constant \( S_0 \) (entropy at \( T = 0 \)), which does not depend on the thermodynamic parameters, does not affect any physical measurement [26]. According to some authoritative experts in the field of thermodynamics, this corresponds to a sufficient condition for implementing (N), not a necessary one [17,15,27]. Problems arising with chemical reactions can be suitably solved [17,15,27]. An analogous position against the necessity of Planck’s restatement appears also in statistical mechanics. E.g. in Ref. [28] statements, according to which systems violating \( S \to 0^+ \) as \( T \to 0^+ \) in the thermodynamic limit, automatically violate (N), have been criticized. Residual entropies coming from theoretical calculations in statistical mechanics, as far as they are not involved with a dependence of the ground state entropy on macroscopic parameters, they still cannot be considered as violations of the third law [28]. Also in Ref. [29] the violation of Planck’s statement is not considered a priori as implying a violation of (N). We first discuss the problem in the framework of the thermodynamics of homogeneous systems; then we add some comments about the relation with statistical mechanics.

Notice that a necessary condition for (N) to hold is that \( S \) is continuous in the limit \( T = 0 \), whichever state is considered on the surface \( T = 0 \). In fact, let us define \( X \equiv x^1, \ldots, x^n \) and let us assume that \( S \) is not continuous in \((0, X_0)\). If this discontinuity is not simply an eliminable one, there exist two different sequences \( \{T_n^{(i)}, X_n^{(i)}\} \), with \( i = 1, 2 \), such that \( (T_n^{(i)}, X_n^{(i)}) \to (0, X_0) \) as \( n \to \infty \) and, moreover, such that

\[
\lim_{n \to \infty} S(T_n^{(1)}, X_n^{(1)}) \neq \lim_{n \to \infty} S(T_n^{(2)}, X_n^{(2)}).
\]

(N) is badly violated. See also sect. VII. The violation of (N) occurs also in the case of a (unnatural) eliminable discontinuity. As a consequence, the continuity of \( S \) on the surface \( T = 0 \) is assumed.

It is to be noted that, if (N) holds, the entropy constant at \( T = 0 \) cannot depend on the composition variables \( n^i \) which specify the number of moles of the component substances which are present in the material whose thermodynamic properties are studied. Herein, we let composition variables \( n^i \) to be included in the set of what we called deformation parameters \(^2\). Then, under suitable hypotheses it holds

\[
\lim_{T \to 0^+} \frac{\partial S}{\partial n^i} = 0.
\]

\(^2\)This choice can be opinable in light of a rigorous axiomatic approach [30], but it allows us to call deformation parameters all the parameters different from \( U \) (from \( T \)) in our discussion, which is limited to some aspects of the third law.
This can be deduced also by means of homogeneity properties of the entropy; for a pure phase at constant $p, T$ one has

\[ S = n \frac{\partial S}{\partial n} \]  

(9)

Moreover, one has for a $k$-components system at constant $p, T$

\[ S(T, V, \ldots, n^1, \ldots, n^k) = \sum_{i=1}^{k} n^i \frac{\partial S}{\partial n^i} \equiv \sum_{i=1}^{k} n^i \bar{S}^i. \]  

(10)

(Note that $\bar{S}^i$ is not the entropy of the single component; such an identification would originate a wrong expression for the entropy, as it is clear for the case of mixtures of ideal gases, where an entropy of mixing appears).

As a consequence, it appears that the arbitrary constant $S_0$ is zero both for pure phases and for mixtures and chemical reactions. In the latter case, the third law states that

\[ \lim_{T \to 0^+} \sum_{i=1}^{k} \nu^i \frac{\partial S}{\partial n^i} = 0 \]  

(11)

where $\nu^i$ are the stoichiometric coefficients. Actually, each derivative should vanish at the absolute zero. The alternative definition of Ref. [27,15] seems to be not satisfactory from the point of view of (N), because the zero-temperature entropy appears to depend on composition variables (which would allow for the composite a different zero-temperature entropy for different molar fractions of the components, against the postulate of Nernst). Then it is thermodynamically appropriate to put $S_0 = 0$. This actually not only does not amount to a real loss of generality, because measurements leave the constant undetermined \(^3\); it is also a necessity (if the third law holds) for homogeneous systems, because $S_0$ is required to satisfy the homogeneity property of the entropy of a homogeneous system. $S$ is an homogeneous function of degree one in the extensive variables, say, $(U, V, N)$. Because of the Euler theorem, this implies that, by introducing the operator

\[ Y \equiv U \frac{\partial}{\partial U} + V \frac{\partial}{\partial V} + N \frac{\partial}{\partial N}, \]  

(12)

the entropy satisfies the equation

\[ Y S = S, \]  

(13)

by inverting

\[ T = \left( \frac{\partial S}{\partial U} \right)^{-1} \equiv g(U, V, N) \]  

(14)

with respect to $U$ [which is allowed by the fact that $\partial T/\partial U > 0$] one finds $U = h(T, V, N)$ which is an homogeneous function of degree one in the extensive variables $(V, N)$. Then one obtains $S(T, V, N)$ which is homogeneous of degree one in the extensive variables $(V, N)$ [it is a quasi-homogeneous function of degree one and weights $(0, 1, 1)$]. If $(N)$ is satisfied, then

\[ \lim_{T \to 0^+} S(T, V, N) = S_0 \]  

(15)

for any choice of $V, N$. Because of the homogeneity, for any $\lambda > 0$ one has

\[ S(\lambda V, \lambda N) = \lambda S(V, N). \]  

\(^{3\text{In order to understand this point, it is important to underline that the constant } S_0 \text{ has actually no operative meaning, in the sense that thermodynamic measurements (and extrapolations for the limit } T \to 0^+ \text{) are relative to the integral of } C/T. \text{ So, in line of principle, it can be put equal to } 0 \text{ without affecting thermodynamic measurements.}}\]
\[
\lim_{T \to 0^+} S(T, \lambda V, \lambda N) = \lambda \lim_{T \to 0^+} S(T, V, N) = \lambda S_0
\] (16)

which is consistent with the independence of the limit from \( V, N \) only for \( S_0 = 0 \). No additive constant can appear as \( T \to 0^+ \), because of the homogeneity, thus Planck’s restatement of the third law is mandatory if \( (N) \) is satisfied.

Summarizing:

Planck’s restatement is mandatory if \( (N) \) holds, due to the homogeneity property of \( S \).

A short comment about the third law in statistical mechanics is in order. It is commonly stated that a violation of \( (N) \) occurs if the ground state is degenerate. Moreover, As far as the limit as \( T \to 0^+ \) is concerned, one has to distinguish between finite size systems and bulk systems. In the latter case, Griffiths shows that, in determining the behavior of thermodynamic systems near the absolute zero, in measurements, what is really important is the contribution of the excitable low-energy quantum states: for bulk systems the contribution of the ground state, at reachable low temperatures, is irrelevant in determining the behavior of the system, which is instead dominated by the contributions of the low-lying energy states [7] (the degeneracy of the ground state is not a good indicator of the behavior of the entropy for bulk systems at low temperature because the thermodynamic limit has to be carried out before the limit as \( T \to 0^+ \) and the two limits in general don’t commute [7]). In statistical mechanics, the ground state degeneracy for bulk systems does not play a straightforward role in determining the behavior as the absolute zero is approached, and examples exist where the ground state is not degenerate but the limit \( S \to 0^+ \) is not implemented [7]. However, a role for the degeneracy of the ground state can be suitably resorted as in Ref. [8]. Therein, it is remarked that the entropy functional at \( T = 0 \) depends on the boundary conditions. Different boundary conditions correspond to different ground states for the bulk system, and the contribution of the excitations of the low-lying states near the absolute zero can be related with a maximally degenerate ground state by means of a variational criterion [8].

We limit ourselves to refer the reader to Ref. [31] for a further approach to the problem of the third law by means of the concept of dynamical entropy and to Ref. [32] for another interesting point of view concerning the problem of the third law in presence of ground state degeneracy.

VI. CARATHÉODORY’S APPROACH AND \( (N) \)

In Carathéodory’s approach [33], the infinitesimal heat exchanged reversibly \( \delta Q_{\text{rev}} \), defined on a open simply connected domain \( D \), is a Pfaffian form, i.e. a one-form \( \omega \), whose integrability has to be ensured in order to define an entropy function. See e.g. Refs. [14,34–37]. This approach appears to be very clarifying with respect to the problem represented by the special surface \( T = 0 \). In the following, we use \( \omega \equiv \delta Q_{\text{rev}} \).

A. Foliation in thermodynamics

Carathéodory’s principle of adiabatic inaccessibility is usually stated for the case where \( D \) has no boundary, that is, \( \partial D = \emptyset \) [36,37]. It can be formulated as follows:

\( (C) \): each neighborhood of any state \( x_0 \) belonging to the domain \( D \) contains states which are inaccessible from \( x_0 \) along solutions of \( \omega = 0 \).

This principle ensures that the Pfaffian form \( \omega \) is completely integrable, i.e. it satisfies \( \omega \wedge d\omega = 0 \), in such a way that a foliation of the thermodynamic manifold into isentropic hypersurfaces is allowed. If a boundary is present, there are some changes in the theory\(^4\). The integrability condition

\[ \omega \wedge d\omega = 0 \] (17)

has to be imposed in the interior of the domain of the differential form \( \omega \), where \( \omega \) is required to be at least \( C^1 \). These properties ensure that Frobenius theorem can be applied and one obtains a foliation in the inner part of the manifold.

\(^4\)The author is indebted to Lawrence Conlon for an enlightening e-mail about the problem of Frobenius theorem for manifolds with boundary.
For what concerns the boundary, it can be in part transverse and in part tangent to the inner foliation. It is tangent when it is a leaf of the foliation itself, i.e. if the boundary is an integral manifold for \( \omega \) [38]. If, instead, it is not a leaf, one can induce on the boundary a foliation from the inner foliation. Then, a foliation of the whole manifold is obtained if sufficient regularity conditions for \( \omega \) on the boundary are assumed.

Let us now consider what happens in thermodynamics. The integrating factor \( T \) vanishes at \( T = 0 \), which means what follows. The non-singular integrable Pfaffian form \( \delta Q_{\text{rev}} \) gives rise to a foliation of the thermodynamic manifold for \( T > 0 \). Each leaf of the foliation is a solution of the equation \( \delta Q_{\text{rev}} = 0 \). This foliation has codimension one (i.e., each leaf is an hypersurface in the thermodynamic manifold). For \( T > 0 \), the leaves of the foliation are the hypersurfaces \( S = \text{const} \). One has then to determine if the surface \( T = 0 \) is a leaf itself. It is indeed an integral submanifold of the Pfaffian form \( \omega \), in the sense that any curve contained in the surface \( T = 0 \). For any initial point lying on the submanifold \( T = 0 \), there is a curve \( \gamma \) lying entirely in the submanifold \( T = 0 \). One has to ensure the uniqueness of the solutions of the Cauchy problem for the ordinary differential equations associated with \( \omega \). The Lipschitz condition for each of them would be enough in order to get an unique solution. If \( \omega \) is \( C^1 \) also on the boundary \( T = 0 \), then we can show that the uniqueness is ensured and \( T = 0 \) is a leaf of the thermodynamic foliation (a tangent leaf). The special leaf \( T = 0 \) cannot intersect any other leaf \( S = \text{const} \) defined at \( T > 0 \), because no intersection of leaves is allowed. In the following subsections, we analyze the above problem in detail.

**B. domain \( \mathcal{D} \)**

Let \( \mathcal{D} \) be the thermodynamic manifold whose independent coordinates are the extensive variables \( U, V, X^1, \ldots, X^n \); the variables \( V, X^1, \ldots, X^n \) will also be called deformation parameters. Assume that \( \dim \mathcal{D} = n + 2 \). \( \mathcal{D} \) is assumed to be an open convex set, in order to match the concavity property of \( S \). Homogeneity requires that \( (\lambda U, \lambda V, \lambda X^1, \ldots, \lambda X^n) \) belongs to \( \mathcal{D} \) for each real positive \( \lambda \), thus \( \mathcal{D} \) has to be also closed with respect to multiplication by a positive real scalar, i.e., \( \mathcal{D} \) has to be a cone. Then, it is natural to require that \( \mathcal{D} \) is a convex cone [39]. One can also relax to some extent the latter condition [e.g., a positive lower bound on \( V, N \) should be introduced on a physical ground, they cannot be arbitrarily near the zero value or statistical fluctuations would not allow to define a meaningful thermodynamic state. Cf. [39]].

**C. Pfaffian forms and homogeneous systems**

Let \( \omega \equiv \delta Q_{\text{rev}} \) be the Pfaffian form of interest, which is identified with the infinitesimal heat exchanged reversibly. It is assumed to be at least of class \( C^1 \) in the inner part of the thermodynamic manifold. One can write

\[
\delta Q_{\text{rev}} = dU + p \, dV - \sum_i \xi_i \, dX^i, \tag{18}
\]

where \( (U, V, X^1, \ldots, X^n) \) are extensive variables. The integrability of \( \delta Q_{\text{rev}} \) ensures that

\[
\delta Q_{\text{rev}} = T \, dS. \tag{19}
\]

We assume that \( \delta Q_{\text{rev}} \) is an homogeneous Pfaffian form of degree one. This means that the vector field

\[
Y \equiv U \frac{\partial}{\partial U} + \frac{\partial}{\partial V} + \sum_i X^i \frac{\partial}{\partial X^i} \tag{20}
\]

is a symmetry for \( \delta Q_{\text{rev}} \) [40,41], in the sense that

\[
L_Y \delta Q_{\text{rev}} = \delta Q_{\text{rev}}, \tag{21}
\]

where \( L_Y \) is the associated Lie derivative. It can be shown that, in the homogeneous case [39], an integrating factor for (18) exists and it is given by

\[
f \equiv i_Y \delta Q_{\text{rev}} = \delta Q_{\text{rev}}(Y) = U + p \, V - \sum_i \xi_i \, X^i. \tag{22}
\]

The integrating factor is required to be such that \( f \neq 0 \), which means that \( Y \) is not a characteristic or trivial symmetry for the distribution associated with \( \delta Q_{\text{rev}} \). Cf. Ref. [41]. Moreover, one requires \( f \geq 0 \), which is easily shown to be equivalent to the conventional choice \( T \geq 0 \). We sketch here some results of Ref. [39]. One finds

10
\[ \delta Q_{\text{rev}} = f \, d\hat{S} \]  

(23)

and it can be shown in general that, for any homogeneous integrable Pfaffian form, \( \omega/f \) has to be equal to \( dH/H \), where \( H \) is a positive definite homogeneous function of degree one; moreover, the homogeneous function \( H \) is unique apart from a multiplicative undetermined constant [39]. This function \( H \) is actually the entropy \( S \), as it can be straightforwardly deduced also by direct comparison with the definition of \( S \) as extensive function

\[ S = \frac{1}{T} U + \frac{p}{T} V - \sum_i \frac{\xi_i}{T} X_i; \]  

(24)

in fact, one finds that \( f \) coincides with the product \( TS \). As a consequence, one has

\[ d\hat{S} = \frac{\omega}{f} = d\frac{S}{S}, \]  

(25)

which implies

\[ S = S_0 \exp(\int_{\Gamma} \frac{\omega}{f}), \]  

(26)

where \( \Gamma \) indicates a path between a reference state \( U_0, V_0, X_{10}, \ldots, X_{n0} \) and the state \( U, V, X^1, \ldots, X^n \). We require that the thermodynamic foliation is described everywhere in \( D \) by the leaves \( \hat{S} = \text{const.} \), which means that \( \hat{S} \) has to be defined everywhere on the thermodynamic manifold (except maybe on the boundary \( f = 0 \)) [39]. The only problems can occur where \( f = 0 \). Moreover, one also assumes that to each level set \( S = \text{const.} \) correspond a unique leaf (which means that each isoentropic surface is path-connected, as it is natural to assume).

**D. zeroes of the integrating factor and the domain**

Let us define the set

\[ Z(f) = \{(U, V, X^1, \ldots, X^n) \mid f(U, V, X^1, \ldots, X^n) = 0\}. \]  

(27)

\( Z(f) \) is the set of the zeroes of \( f \). We define also

\[ Z(T) = \{(U, V, X^1, \ldots, X^n) \mid T(U, V, X^1, \ldots, X^n) = 0\}, \]  

(28)

and

\[ Z(S) = \{(U, V, X^1, \ldots, X^n) \mid S(U, V, X^1, \ldots, X^n) = 0\}. \]  

(29)

The set \( Z(f) = Z(T) \cup Z(S) \) corresponds to an integral manifold of \( \omega \) (\( \omega \) is non-singular and \( \omega = f d\hat{S} \)).

1. **Z(T)**

The set \( Z(T) \) is expected to be an hypersurface, but, in general, it could be a priori a submanifold of dimension \( 1 \leq k \leq n + 1 \). Actually, it is natural to assume that it is a hypersurface, i.e., a manifold of codimension one. The equation

\[ T(U, V, X^1, \ldots, X^n) = 0 \]  

(30)

is required to be implemented for any value of \( V, X^1, \ldots, X^n \) which is compatible with the system at hand. Contrarily, one should admit that \( T = 0 \) could be allowed only for a restricted region of parameters (e.g., a crystal could not be allowed to assume a value \( V = V_0 \) for the volume at \( T = 0 \)) in such a way that a thermal contact with a lower temperature system could not lower the system temperature near the absolute zero if values of the parameters outside the allowable range would be involved. We then assume that the \( T = 0 \) is a path-connected hypersurface which coincides with the adiabatic boundary \( T = 0 \) of the thermodynamic manifold. See also subsect. VII F.
The set $Z(S)$ has to be contained in the boundary of the thermodynamic manifold. This is a consequence of the concavity of $S$ and of the requirement $S \geq 0$, as it is shown in sect. VII. $S = 0$ can be moreover attained only on the boundary surface $T = 0$, in fact $S = 0$ at $T > 0$ can be rejected on physical grounds. In fact, any state $z$ such that $T_z > 0$ and $S(z) = 0$ should have the peculiar property to allow the system only to absorb heat along any path $\gamma_z$ starting from $z$ in a neighborhood $W_z$ of $z$. If $C_{\gamma}(T)$ is the heat capacity along a path $\gamma$ which does not contain isothermal sub-paths, one has that

$$S(y) = \int_{T_z}^{T_y} \frac{dT}{T} C_{\gamma_z}(T)$$

(31)

should be positive for any state $y$ non isoentropic to $z$ in $W_z$, which is possible only for heat absorption (in fact, $C_{\gamma_z}(T) < 0$ would be allowed for states such that $T_z < T_y$, which would imply heat absorption, and $C_{\gamma_z}(T) > 0$ would be allowed for states such that $T_z > T_y$). The same is true if one considers an isothermal path starting at $z$, in fact the heat exchanged would be $T_z \Delta S$ and $\Delta S$ should be positive in a neighborhood of $z$, being $S = 0$ a global minimum of $S$. Thermal contact with a colder body at $T < T_z$ should allow an heat flow outgoing from the system because of the second law in Clausius formulation. Then, no possibility to approximate such a thermal contact by means of a reversible transformation exists, and this behavior can be refused as pathological.

There is also another argument one can introduce against the possibility that, for a non-negative definite entropy, the set $Z(S) - Z(T)$ is non-empty. By using standard formulas of thermodynamics, one has

$$S(T, x^1, \ldots, x^{n+1}) = S(0, x^1, \ldots, x^{n+1}) + \int_0^T \frac{dz}{z} C_{x^1,\ldots,x^{n+1}}(z) > 0 \quad \forall T;$$

(32)

Then a non-negative concave entropy implies that the set $Z(S)$ of the zeroes of $S$ is contained in the set $Z(T)$ of the zeroes of $T$:

$$Z(S) \subseteq Z(T).$$

(33)

The two sets coincide if (N) holds, otherwise $Z(S) \subset Z(T)$ and it could be that $Z(S) = \emptyset$. Then we get the following equality:

$$Z(f) = Z(T).$$

(34)

If one considers a concave entropy which can be also negative, then it happens that $Z(f) \supseteq Z(T)$ because $Z(S)$ is not, in general, a subset of $Z(T)$. A typical example is the classical ideal gas. Let us consider the monoatomic ideal gas. One has [48]

$$S(U, V, N) = N \left[ \frac{5}{2} + \log \left( \frac{U^{3/2} V}{N^{5/2}} \frac{1}{(3 \pi)^{3/2}} \right) \right];$$

(35)

the corresponding Pfaffian form is

$$\omega = dU + \frac{2}{3} \frac{U}{V} dV + \frac{2}{3} \frac{U}{N} \log \left( \frac{U^{3/2} V}{N^{5/2}} \frac{1}{(3 \pi)^{3/2}} \right) dN$$

(36)

and one has

$$T = \frac{2}{3} \frac{U}{N},$$

(37)

and

$$f = \frac{2}{3} U \left[ \frac{5}{2} + \log \left( \frac{U^{3/2} V}{N^{5/2}} \frac{1}{(3 \pi)^{3/2}} \right) \right].$$

(38)

In this case one has
E. $T = 0$ in thermodynamics

The equation $f = 0$ is an implicit equation which defines a submanifold of the thermodynamic manifold. This is trivial if $f$ is at least $C^1$ everywhere in $D \cup \partial D$, in fact $f = 0$ defines a $C^1$ hypersurface contained in the domain. This submanifold could be trivially an hyperplane $U = C_0 = \text{const.}$, or a non-trivial hypersurface $U = b(U, V, X^1, \ldots, X^n)$. A further discussion is found in subsect. VI F and in subsect. VII C.

F. boundary revisited

In thermodynamics, as discussed in sect. VID, it is to some extent natural to assume that the boundary $T = 0$ is described explicitly by a (maybe smooth, let us assume at least $C^1$) function:

$$ U = b(X^1, \ldots, X^{n+1}); \quad (41) $$

one can figure that it corresponds to the equation for the ground-state energy of the system as a function of the deformation parameters, as it is clear from the following analysis. $b$ is a function which is homogeneous of degree one with respect to $(X^1, \ldots, X^{n+1})$:

$$ b(\lambda X^1, \ldots, \lambda X^{n+1}) = \lambda b(X^1, \ldots, X^{n+1}). \quad (42) $$

Thus, $b$ has to be defined on a cone $\mathcal{K}_b \subset \mathbb{R}^{n+1}$. Moreover, if $U_0, X^1, \ldots, X^{n+1}$ belongs to the boundary $T = 0$, from

$$ T(U, X^1, \ldots, X^{n+1}) = \int_{U_0}^{U} dU \frac{\partial T}{\partial U}(U, X^1, \ldots, X^{n+1}), \quad (43) $$

where the integral is an improper integral, because $\partial T / \partial U = 1/C_{X^1, \ldots, X^{n+1}} \to \infty$ as $T \to 0^+$, and from the concavity of $S$, which implies that $C_{X^1, \ldots, X^{n+1}} > b$, one finds that $U > U_0$, i.e. it has to hold $U \geq b(X^1, \ldots, X^{n+1})$. Thus, the domain $\mathcal{D}$ has to be such that the inequality $U \geq b(X^1, \ldots, X^{n+1})$ is implemented for each $U$ and for each $(X^1, \ldots, X^{n+1}) \in \mathcal{K}_b$. The domain $\mathcal{D}$ contains the set

$$ Z(T) = \{ U = 0 \} \quad (39) $$

and

$$ Z(S) = \{ (U, V, N) \mid \frac{U^{3/2} V}{N^{5/2}} \cdot \frac{1}{(3 \pi)^{3/2}} = \exp \left( -\frac{5}{2} \right) \}. \quad (40) $$

Then $Z(f) \supset Z(T)$ and $f$ vanishes before $U = 0$ is reached.
This set is the so-called epigraph of the function \( b \). If the function \( b(V,X^1,\ldots,X^n) \) is required to be convex, then it is defined on the convex cone \( \mathcal{K}_b \), and its epigraph \( \text{epi}(b) \) is a convex cone (the epigraph of an homogeneous \( b \) is a cone). Then, the domain \( \mathcal{D} \) can be chosen to be

\[
\mathcal{D} = \text{epi}(b).
\]

One can also assume that \( \mathcal{D} \) is a convex cone of the form

\[
\mathcal{D} = \{(U,V,X^1,\ldots,X^n) \mid (V,X^1,\ldots,X^{n+1}) \in \mathcal{K}_b, U \geq b(V,X^1,\ldots,X^n)\},
\]

where the intervals \( I_V, I_{X^1}, \ldots, I_{X^n} \) are \( \mathbb{R}_+ \). We can find a coordinatization of the boundary by means of coordinates \((B,X^1,\ldots,X^{n+1})\) such that the boundary \( T = 0 \) coincides with \( B = 0 \). In fact, we can simply define

\[
B = U - b(X^1,\ldots,X^{n+1});
\]

\( B \geq 0 \) is a degree one homogeneous function, and \( \partial U / \partial B = 1 \). By inverting one finds

\[
U = B + b(X^1,\ldots,X^{n+1}).
\]

As a consequence, one gets

\[
\bar{f} \equiv f(B,X^1,\ldots,X^{n+1}) = B + b(X^1,\ldots,X^{n+1}) - \sum_k \xi_k X^k;
\]

by definition, \( \bar{f} \) vanishes for \( B = 0 \), i.e.

\[
0 = b(X^1,\ldots,X^{n+1}) - \sum_k \xi_k(0,X^1,\ldots,X^{n+1}) X^k
\]

\[
\iff \frac{\partial b}{\partial X^k} = \xi_k(0,X^1,\ldots,X^{n+1}) \ \forall k.
\]

Notice that, by defining for all \( i = 1,\ldots,n+1 \)

\[
\tilde{\xi}_i(B,X^1,\ldots,X^{n+1}) \equiv \xi_i(B,X^1,\ldots,X^{n+1}) - \frac{\partial U}{\partial X^i}(B,X^1,\ldots,X^{n+1}),
\]

one finds

\[
\omega = dB - \sum_i \tilde{\xi}_i(B,X^1,\ldots,X^{n+1}) dX^i,
\]

and it holds \( \tilde{\xi}_i(B = 0,X^1,\ldots,X^{n+1}) = 0 \) for all \( i = 1,\ldots,n+1 \), because of the definition for \( f = 0 \) to be an integral hypersurface for \( \omega \). Moreover, notice that, under this assumption about the boundary \( T = 0 \), one obtain that \( Z(S) \subseteq Z(T) \) necessarily. In fact, one can write for an everywhere continuous entropy

\[
S(B,X^1,\ldots,X^{n+1}) = S(0,X^1,\ldots,X^{n+1}) + \int_0^B dY \frac{1}{T(Y,X^1,\ldots,X^{n+1})},
\]

where \( S(0,X^1,\ldots,X^{n+1}) \) is the value attained by \( S \) at \( B = 0 \) by continuity; it is evident that \( S \) cannot vanish outside \( Z(T) \), because \( S(0,X^1,\ldots,X^{n+1}) \geq 0 \) and \( \int_0^B dY 1/T(Y,X^1,\ldots,X^{n+1}) > 0 \) for all \( B > 0 \).

As far as the entropy \( S \) as a function of \( B,X^1,\ldots,X^{n+1} \) is concerned, it is such that

\[
\frac{\partial S}{\partial B} = \frac{1}{T(B,X^1,\ldots,X^{n+1})},
\]

\[
\frac{\partial S}{\partial X^i} = -\frac{\tilde{\xi}_i(B,X^1,\ldots,X^{n+1})}{T(B,X^1,\ldots,X^{n+1})} \ \forall i = 1,\ldots,n+1.
\]
One could also allow for different choices of coordinates. Instead of $B$ defined as above, one could introduce another (maybe local) coordinate for the boundary $f = 0$, say $\hat{B}$, such that the boundary coincides with $\hat{B} = 0$. The coordinate transformation $U \mapsto \hat{B}$ is required to be regular, i.e.

$$\frac{\partial U}{\partial \hat{B}} \neq 0 \quad \text{for} \quad \hat{B} = 0$$

(57)

$$\frac{\partial \hat{B}}{\partial U} \neq 0 \quad \text{for} \quad \hat{B} = 0,$$

(58)

then one can find

$$\omega = \frac{\partial U}{\partial \hat{B}} d\hat{B} - \sum_i \hat{\xi}_i(\hat{B}, X^1, \ldots, X^{n+1}) dX^i,$$

(59)

where

$$\hat{\xi}_i(\hat{B}, X^1, \ldots, X^{n+1}) = \xi_i(\hat{B}, X^1, \ldots, X^{n+1}) - \frac{\partial U}{\partial X_i}(\hat{B}, X^1, \ldots, X^{n+1}),$$

(60)

and

$$\hat{f} = \frac{\partial U}{\partial \hat{B}} \hat{B} - \sum_i \hat{\xi}_i(\hat{B}, X^1, \ldots, X^{n+1}) X^i.$$  

(61)

It is important to point out that, also in these coordinates, one has

$$\hat{\xi}_i(\hat{B} = 0, X^1, \ldots, X^{n+1}) = 0.$$  

(62)

In the following, we define

$$\frac{\partial U}{\partial \hat{B}} \equiv a(\hat{B}, X^1, \ldots, X^{n+1}).$$

(63)

Notice that, because of the properties of the Pfaffian form $\omega$, the absolute temperature $T$ cannot be used as a good coordinate for the boundary, in fact $\partial U/\partial T \to 0$ as $T \to 0^+$ for all physical systems allowing a finite $S$ at $T = 0$. This choice (as well as the choice of $f$) seems to transform the regular Pfaffian form $\omega$ into a singular one, but this trouble is simply due to the singularity in the jacobian of the coordinate transformation $U \mapsto T$, which is a diffeomorphism only for $T > 0$. See also [19].

**G. condition to be satisfied in order that $T = 0$ is a leaf**

In order to understand better the problem of the boundary $T = 0$, it is useful to recall the equivalence between the equation $\omega = 0$ and the so-called Mayer-Lie system of partial differential equations [herein, $X^1$ stays for any extensive variable different from $U$ and $\xi_i$ for the corresponding intensive variable]

$$\frac{\partial U}{\partial X_i}(X^1, \ldots, X^{n+1}) = \xi_i(U, X^1, \ldots, X^{n+1}) \quad \text{for} \quad i = 1, \ldots, n + 1.$$  

(64)

One can also assign an initial condition

$$U(X_0^1, \ldots, X_0^{n+1}) = U_0$$  

(65)

and thus define a Cauchy problem for the above Mayer-Lie system. The integrability condition $\omega \wedge d\omega = 0$ in the inner part of the manifold is sufficient for a $C^1$ Pfaffian form in order to ensure the existence and the uniqueness of the above Cauchy problem. This means that the Cauchy problem with initial point on the $T = 0$ boundary allows solutions which lie in $T = 0$. If $\omega$ is $C^1$ also on the boundary, then it is evident that the aforementioned curves are the only possible solutions to the above Cauchy problem with initial point on the surface $T = 0$. In other terms, if $\omega \in C^1$ everywhere, then $T = 0$ is a leaf of the thermodynamic foliation. But, a priori, one can consider also a Pfaffian form $\omega$ such that it is continuous on the boundary $T = 0$ but non-necessarily $C^1$ there. The uniqueness of the solution
of (64) with initial condition on the surface \( T = 0 \) could be ensured if the functions \( \xi_i(U, X^1, \ldots, X^{n+1}) \) are locally Lipschitzian with respect to \( U \) uniformly with respect to \( X^1, \ldots, X^{n+1} \) in a neighborhood of \((U_0, X^1_0, \ldots, X^{n+1}_0)\). If even this condition fails, then the continuity of \( \omega \), i.e., the continuity of \( \xi \) also in \( T = 0 \) can allow multiple solutions of the differential equation (64).

Let us consider the following differential equation which describes isentropic curves in the special coordinated adapted to the boundary introduced in the previous subsection:

\[
\frac{dB}{d\tau} = \sum_i \xi_i(B(\tau), X^1(\tau), \ldots, X^{n+1}(\tau)) \frac{dX^i}{d\tau} \tag{66}
\]

This equation can be easily obtained from (64). Let us consider at least piecewise \( C^1 \) functions \( X^1(\tau), \ldots, X^{n+1}(\tau) \) for \( \tau \in [0, 1] \). These functions are arbitrarily assigned. Let us consider a solution curve such that \( \lim_{\tau \to \tau_0} B(\tau) = 0 \) for \( \tau_0 \in [0, 1] \). By hypothesis, \( X^1(\tau), \ldots, X^{n+1}(\tau) \) are finite for \( \tau \to \tau_0 \). Then, by continuity, such a solution can be extended to \( \tau = \tau_0 \), i.e., \( T = 0 \) cannot be a leaf. This happens as a consequence of well-known theorems on the ordinary differential equations, see [45], pp. 67-68. Let us then consider a point \((B(0) = 0, X^1(0) = X^1_0, \ldots, X^{n+1}(0) = X^{n+1}_0)\) on the surface \( T = 0 \). In each neighborhood of this point, one can find inner points, each of which belongs to a surface \( S = \text{const.} \). In fact, each point of the surface \( B = 0 \) is a limit point for the nearby inner points of the thermodynamic domain and each inner point has to belong to a \( S = \text{const.} \) integral manifold, because of the integrability condition. If \( T = 0 \) is a leaf [or if the connected components of \( T^{-1}(0) \) are leaves if \( T = 0 \) is not connected], the only possibility is that, in approaching \( T = 0 \), one is forced to change leaf \( S = \text{const.} \), i.e., it is not possible to approach \( T = 0 \) by remaining on the same leaf \( S = \text{const.} \), otherwise the inner solution of \( \omega = 0 \) could be extended to \( T = 0 \). Notice that, in case there exist two solutions of the Cauchy problem for the differential equation (66) with initial condition \((B(0) = 0, X^1(0) = X^1_0, \ldots, X^{n+1}(0) = X^{n+1}_0)\), one lying in the \( T = 0 \) surface and the other leaving the \( T = 0 \) surface, then these solutions are tangent at the initial point. This means that, in case of existence of the limit as \( B \to 0^+ \) of the entropy, when \( (N) \) is violated, there are surfaces \( S = \text{const.} \) which are tangent to the submanifold \( T = 0 \). We now prove these statements.

1. validity of \( (N) \)

If \( (N) \) holds, then \( T = 0 \) plays at most the role of asymptotic manifold for the inner leaves \( S = \text{const.} \). No inner integral manifold can intersect \( T = 0 \), i.e., \( T = 0 \) is a leaf. In order to approach \( T = 0 \) at finite deformation parameters, one has necessarily to change from one adiabatic surface \( S = \text{const.} \) to another one, it is impossible to approach \( T = 0 \) by means of a single adiabatic transformation. We have then a mathematical explanation of the naive unattainability picture sketched by means of standard textbooks on thermodynamics (cf. also the definition of \( P(x) \) transformations in [2]).

2. violation of \( (N) \)

If, instead, \( (N) \) is violated and \( \lim_{B \to 0^+} S(B, X^1_0, \ldots, X^{n+1}_0) = S(0, X^1_0, \ldots, X^{n+1}_0) \), then the inner integral manifold \( S(0, X^1_0, \ldots, X^{n+1}_0) = \text{const.} \) exists and can be continuously extended to \( T = 0 \). This can be proved by means of a variant of the implicit function theorem. For simplicity, we put here

\[
X \equiv X^1, \ldots, X^{n+1}. \tag{67}
\]

Let us consider a point \((0, X_0)\) which is not a local minimum for \( S \), i.e. it is not such that \( S(0, X_0) \leq S(B, X) \) in a neighborhood of \((0, X_0)\). Such a point surely exists if \( (N) \) is violated, as it is easy to show (cf. also [19]). We are interested in the zeroes of the function

\[
\sigma(B, X) \equiv S(B, X) - S(0, X_0). \tag{68}
\]

The function \( \sigma(B, X) \) is a continuous function which is monotonically strictly increasing in \( B \) everywhere in the domain \( \mathcal{D} \cup \partial \mathcal{D} \), because \( S(B, X) \) is, by construction, a strictly increasing monotone function in \( B \), as it is evident from (54).

In particular, we wish to know if there is a continuous function \( B(X) \) defined in a neighborhood of \((0, X_0)\) such that \( \sigma(B(X), X) = 0 \) and such that \( B(X_0) = 0 \). If \((0, X_0)\) is a strict local minimum for \( S \), then by definition there exists a neighborhood of \((0, X_0)\) where \( \sigma(B, X) > 0 \), thus the aforementioned function \( B(X) \) does not exists. If it is a weak local
minimum, in the sense that \( S(0, X_0) \leq S(B, X) \) in a neighborhood and the equality is allowed, again \( \sigma(B(X), X) = 0 \) does not admit solutions, in fact if \( S(B, X) = S(0, X_0) \) is allowed in a neighborhood \( W \supset [0, B_0] \times V \) of \((0, X_0)\), with \( V \ni X_0 \) open set, then \( S(0, X) < S(0, X_0) \) because \( S(0, X) < S(B, X) \). Thus, being \((0, X_0)\) a local minimum, one can find a smaller neighborhood where \( S(B, X) = S(0, X_0) \) is impossible for any \( B > 0 \) \((S(0, X) = S(0, X_0)\) is instead allowed).

Notice that \((0, X_0)\) cannot be a local but non global minimum for \( S \) under the natural requirement that each surface \( S = \text{const.} \) corresponds to a unique integral manifold of \( \delta Q_{rev} \) [this means that isentropic states are path-connected. Cf. [39].] In fact, in homogeneous thermodynamics, there exists an integral manifold of \( \delta Q_{rev} \) such that \( S(B, X) = S(0, X_0) = \text{const.} \) if \((0, X_0)\) is not a global minimum, and to such an integral manifold \((0, X_0)\) would not belong if \((0, X_0)\) is a local minimum. Notice also that no point belonging to the boundary \( B = 0 \) can be a local maximum, because \( S(B, X) \) is a strictly increasing monotone function in \( B \).

In any convex neighborhood \( W \) of \((0, X_0)\) there exist \((B^+, X^+)\) and \((B^-, X^-)\) such that \( \sigma(B^+, X^+) > 0 \) and \( \sigma(B^-, X^-) < 0 \), because \((0, X_0)\) is not a local minimum. By continuity, for any convex neighborhood of \((0, X_0)\) there exists \((B^0, X^0)\) such that \( \sigma(B^0, X^0) = 0 \). The point \((0, X_0)\) is then a limit point for the set \( Z(\sigma) \equiv \{(B^0, X^0) | \sigma(B^0, X^0) = 0\} \), which is a closed set because \( \sigma \) is continuous. In order to show that a solution \( B(X) \) for \( \sigma(B(X), X) = 0 \) exists and is unique, we introduce the following auxiliary function

\[
\tilde{\sigma}(B, X) \equiv \begin{cases} 
\sigma(B, X) & \text{for } B \geq 0; \\
S(0, X) - S(0, X_0) + B & \text{for } B < 0.
\end{cases}
\]

This function \( \tilde{\sigma}(B, X) \) is a continuous function which is monotone strictly increasing in \( B \) also for \( B < 0 \). We have extended then \( \sigma \) to negative values of \( B \), which is shown to be an useful trick. We cannot use the standard form of the implicit function theorem because \( \partial S/\partial B \) diverges at \( B = 0 \). Nevertheless, the proof is a variant of the standard proof of the implicit function theorem for scalar functions. We have that \( \tilde{\sigma}(0, X_0) = 0 \). By the monotonicity property one has that there exist \( B_1 < 0 < B_2 \) such that \( \tilde{\sigma}(B_1, X_0) < 0 < \tilde{\sigma}(B_2, X_0) \). By continuity, there exists an open neighborhood \( R \ni X_0 \) such that \( \tilde{\sigma}(B_1, X) < 0 < \tilde{\sigma}(B_2, X) \) for all \( X \in R \). Then, from the intermediate value theorem it follows that there exists a value \( B \in (B_1, B_2) \) such that \( \tilde{\sigma}(B, X) = 0 \) for any fixed \( X \in R \). Monotonicity ensures that \( \bar{B} \) is unique for each fixed \( X \in R \). The function \( B(X) : R \to \mathbb{R} \) is then defined as the map defined by \( B(X) = \bar{B} \), where \( \bar{B} \) is the solution of \( \tilde{\sigma}(B, X) = 0 \) for each fixed \( X \in R \). Such a function satisfies \( B(X_0) = 0 \) and is also continuous in \( X \). This follows again from the fact that \( \tilde{\sigma} \) is a continuous function which is monotonically strictly increasing in \( B \). Being continuous, one has that the set

\[
Z(\tilde{\sigma}) \equiv \{(B, X) | \tilde{\sigma}(B, X) = 0\}
\]

is a closed set. Given a sequence \( \{X_n\} \subset R \) such that \( X_n \to \bar{X} \in R \) for \( n \to \infty \), one finds that there exists a unique (by monotonicity) \( \hat{B} \) such that \( (\hat{B}, \bar{X}) \in Z(\tilde{\sigma}) \). This means that \( \lim_{n \to \infty} B(X_n) = B(\bar{X}) = \hat{B} \), i.e., \( B(X) \) is continuous.

It is evident that

\[
Z(\tilde{\sigma}) \supseteq Z(\sigma)
\]

and we have to get rid of the spurious solution \( B = -(S(0, X) - S(0, X_0)) < 0 \) which could occur for \( S(0, X) - S(0, X_0) > 0 \). But this solution cannot hold for any \( X \in R \), because in any neighborhood of \((0, X_0)\) there exist points \((0, X^-)\) such that \( S(0, X^-) - S(0, X_0) < 0 \). Thus, being the spurious solution not defined in the whole \( R \), the above theorem allows to conclude that \( B(X) \geq 0 \) surely exists.

Notice that, for inner points \( B(X) > 0 \), this solution is actually a leaf of the foliation defined by the integrable at least \( C^1 \) Pfaffian form \( \omega \). As a consequence, for inner points \( B(X) \) is at least \( C^2 \). One can also calculate the gradient of \( B(X_1, \ldots, X^{n+1}) \):

\[
\left( \frac{\partial B}{\partial X^1}, \ldots, \frac{\partial B}{\partial X^{n+1}} \right) = \left( \tilde{\xi}_1, \ldots, \tilde{\xi}_{n+1} \right),
\]

where the latter equality is due to the fact that \( B(X) \) satisfies the Mayer-Lie system. It is then evident that

\[
\left( \frac{\partial B}{\partial X^1}, \ldots, \frac{\partial B}{\partial X^{n+1}} \right) \to 0 \quad \text{for } B \to 0^+,
\]

i.e. \( B(X) \) reaching \( B = 0 \) is tangent to \( B = 0 \).
The above condition about the absence of inner integral manifolds arbitrarily approaching $T = 0$ is also sufficient. Notice also that it does not forbid the inner leaves to asymptotically approach $T = 0$ as some deformation variable, say $X_k$, is allowed to diverge: $|X_k| \to \infty$ as $B \to 0^+$. The unattainability is clearly ensured because of such a divergence. Let us consider the following equation:

$$\sum_{i=1}^{n+1} \xi_i(B, X^1(B), \ldots, X^{n+1}(B)) \frac{dX_i}{dB} - 1 = 0,$$  \hspace{1cm} (74)

which is another rewriting of the above equation where $B$ plays the role of independent variable and where $n$ functions $X^i$, say $X^1(B), \ldots, X^n(B)$, are arbitrarily assigned. For simplicity, let us put $X^{n+1}(B) \equiv X(B)$. One could also consider $X^1 = X^1_0, \ldots, X^n = X^n_0 = \text{const}$. Then, one obtains

$$\frac{dX}{dB} = \frac{1}{\xi_{n+1}(B, X(B); X^1_0, \ldots, X^n_0)}.$$  \hspace{1cm} (75)

It is evident from our discussion above that any solution $X(B)$ has to be such that $|X(B)| \to \infty$ when $B \to 0^+$ if $T = 0$ has to be a leaf. Some examples are given below.

3. examples

Let us consider

$$\omega = dU + \frac{2}{3} U \frac{dV}{V} dV;$$  \hspace{1cm} (76)

the domain is chosen to be $0 \leq U, 0 < V$ and the Pfaffian form $\omega$ is $C^1$ everywhere. One has

$$f = \frac{5}{3} U$$  \hspace{1cm} (77)

which vanishes for $U = 0$. The boundary $U = 0$ is an integral submanifold of $\omega$. Let us consider the Cauchy problem

$$\frac{dU}{dV} = -\frac{2}{3} \frac{U}{V}$$  \hspace{1cm} (78)

$$U(V_0) = 0.$$  \hspace{1cm} (79)

It is evident that the only solution of this problem is $U = 0$, which is a leaf of the thermodynamic foliation. By integrating, one finds the (concave) entropy $S = c_0 \frac{U^{3/5} V^{2/5}}{V}$ and $T = 5/(3c_0) \left(\frac{U}{V}\right)^{2/5}$ [c_0 is an undetermined constant]. (N) is satisfied. Along an isoentropic surface $S_0 > 0$, one finds

$$U = \left(\frac{S_0}{c_0}\right)^{5/3} V^{-2/3}$$  \hspace{1cm} (80)

and $T = 0$, i.e. $U = 0$ can be approached only for $V \to \infty$.

Let us consider a Pfaffian form having the same domain $0 \leq U, 0 < V$

$$\omega = dU + \left(\frac{U}{V}\right)^{2/3} dV;$$  \hspace{1cm} (81)

the Pfaffian form $\omega$ is not $C^1$ on the boundary $U = 0$. One has

$$f = U + U^{2/3} V^{1/3}$$  \hspace{1cm} (82)

which vanishes for $U = 0$. The Cauchy problem

$$\frac{dU}{dV} = -\left(\frac{U}{V}\right)^{2/3}$$  \hspace{1cm} (83)

$$U(V_0) = 0.$$  \hspace{1cm} (84)
allows two solutions:

\[ U = 0 \]  

and

\[ U = (V_0^{1/3} - V^{1/3}). \]  

The latter solution holds for \( 0 < V \leq V_0 \), and it can be easily identified with the isoentrope \( S = S_0 = c_0 V_0 \), where \( S = c_0(U^{1/3} + V^{1/3})^3 \) is the (concave) entropy. (N) is violated and the two solutions are tangent for \( U = 0 \).

Let us consider the following example, which is inspired to the low-temperature behavior of a Fermi gas. The Pfaffian form one takes into account is

\[ \omega = dU + \frac{2}{3} \frac{U}{V} dV - \left( -\frac{1}{3} \frac{U}{N} + 2c (NV)^{2/3} \right) dN, \]  

where \( c \) is a positive constant. This Pfaffian form is integrable and the integrating factor is

\[ f = 2U - 2c \frac{N^{5/3}}{V^{2/3}}. \]  

Then the zero of the integrating factor occurs for

\[ U = c \frac{N^{5/3}}{V^{2/3}}, \]  

and, by construction, being \( f \geq 0 \), one imposes \( U \geq b(V, N) \equiv c \frac{N^{5/3}}{V^{2/3}} \). The function \( b(V, N) \) is extensive and convex. Let us define

\[ B = U - c \frac{N^{5/3}}{V^{2/3}}. \]  

This coordinate transformation is regular in \( B = 0 \). We have

\[ \bar{p}(B, V, N) = \frac{2}{3} \frac{B}{V}, \]  

\[ \bar{\mu}(B, V, N) = -\frac{1}{3} \frac{B}{N}, \]  

and

\[ \bar{f} = 2B. \]  

Then, one finds

\[ S = \alpha B^{1/2} V^{1/3} N^{1/6}, \]  

(\( \alpha \) is a proportionality constant) which can be easily re-expressed in terms of \( (U, V, N) \):

\[ S = \alpha \left( UV^{2/3} N^{1/3} - cN^2 \right)^{1/2}. \]  

Notice that, along \( S = S_0 = \text{const.} \) one has

\[ B = \left( \frac{S_0}{\alpha} \right)^2 \frac{1}{V^{2/3} N^{1/3}}, \]  

which can approach \( B = 0 \) only for \( V \to \infty \) and/or \( N \to \infty \). Moreover,

\[ T = \frac{2}{\alpha} \left( UV^{2/3} N^{1/3} - cN^2 \right)^{1/2} N^{-1/3} V^{-2/3}, \]  

and \( \partial T/\partial U \) diverges as \( T \to 0^+ \).
We can show, by means of purely thermodynamic considerations, that:

in Gibssian variables, if the homogeneous Pfaffian form is (at least) $C^1$ also on the boundary $Z(f)$ and if the entropy $S$ is concave, then (N) holds.

(sufficient but not necessary condition)

Recall that $S \geq 0$ by construction and also on statistical mechanical grounds. Let us assume that the Pfaffian form $\delta Q_{\text{rev}}$ is $C^1$ everywhere, also on the boundary, and that it satisfies the integrability condition in the inner part of the manifold. Then, the integrating factor $f$ is a $C^1$ function everywhere. In variables $U, V, N$ one has

$$f = U + p(U, V, N) V - \mu(U, V, N) N$$

where $p, \mu$ are $C^1$. Consider

$$\frac{\partial f}{\partial U} = 1 + S \frac{\partial T}{\partial U}.$$  \hfill (99)

$S$ cannot be non-negative and concave near $T = 0$ if it diverges as $T \to 0^+$ [2]. See also sect. VII. Then concavity and positivity also near $T = 0$ force the entropy to be finite in the limit $T \to 0^+$. Moreover, one has $\partial T/\partial U = 1/C_{X^1, \ldots, X^n}$, where $C_{X^1, \ldots, X^n}$ is the standard heat capacity at constant deformation parameters, which has to vanish in the limit as $T \to 0^+$ because $S$ has to be finite in that limit. As a consequence, $\partial T/\partial U = 1/C_{X^1, \ldots, X^n} \to \infty$ as $T \to 0^+$. Then, by inspection of (99), it is evident that $f$ is $C^1$ also on the boundary only for $S \to 0^+$ as $T \to 0^+$. As a consequence of this theorem, we can conclude that any violation of (N) is involved with a Pfaffian form that is not $C^1$ also on the boundary, as it can be easily verified by considering the examples violating (N) in section VII.

1. geometrical aspects of $f = 0$

If $\delta Q_{\text{rev}}$ is at least of class $C^1$ everywhere, then $d(\delta Q_{\text{rev}})$ is continuous and finite on the surface $f = 0$ (that is, $T = 0$). From a geometrical point of view, the surface $f = 0$ is a so-called separatrix according to the definition of Ref. [40], in the sense that the 2–form $(\delta Q_{\text{rev}}) \wedge df$ vanishes with $f$ on this surface. One has $(\delta Q_{\text{rev}}) \wedge df = -f d(\delta Q_{\text{rev}})$, as it can be easily verified by using (21) and standard Cartan identities. $f = 0$ is also a surface where the symmetry associated with the vector field $Y$ becomes trivial [41], in the sense that it becomes tangent to the submanifold $f = 0$. In the case where the complete integrability of $\delta Q_{\text{rev}}$ is preserved also on the surface $f = 0$, one has that $f = 0$ appears as a special leaf of the thermodynamic foliation, it is indeed the only leaf which is left invariant by the action of $Y$.

In general, for a sufficiently regular $\omega$ at $f = 0$, the property for $f = 0$ to be a separatrix in the sense of Ref. [40] ensures that the solutions of $\delta Q_{\text{rev}} = 0$ in the inner part of the thermodynamic manifold cannot intersect the integral submanifold $f = 0$. Then, the integral manifold $f = 0$ is a leaf of the foliation defined by $\delta Q_{\text{rev}}$ if it is also a separatrix. Moreover, it is a special leaf, being a separatrix.

We have shown above that $S \to 0^+$ as $f \to 0^+$ for $\omega \in C^1$ everywhere. We can note that, if the condition for $\delta Q_{\text{rev}}$ to be $C^1$ also on $f = 0$ is relaxed, then the condition

$$\lim_{f \to 0^+} f d(\delta Q_{\text{rev}}) = 0$$

is not sufficient for ensuring (N). A simple counterexample is given by

$$\omega = dU + \left( \frac{U}{V} \right)^{\frac{2}{3}} dV$$

where $0 \leq U, 0 < V_1 < V$ and where $f d\omega$ vanishes as $f \to 0^+$ but (N) is violated.

The requirement that $\omega$ is $C^1$ everywhere is, at the same time, too restrictive. In fact, it is evident that the following homogeneous Pfaffian form, defined for $D \equiv \{0 \leq U < V/\epsilon^2, \ V > 0\}$

$$\omega = dU + p(U, V) \ dV,$$

is
Notice that (HOM) is not affected by the connectedness properties of $f$.

If $S$ has only to check if the above integral diverges along any rectifiable curve approaching the surface $S$ and concave entropy cannot diverge (cf. sect. VII). Thus, once ensured the concavity property for $f$, where $\alpha > 0$ and $\beta < 0$ are constants and the domain is restricted by $V/N \geq -\beta_0/\alpha_0$. Then one has

$$f = 3 U + \alpha_0 \frac{(U V)^{2/3}}{N^{1/3}} + \beta_0 \frac{(U N)^{2/3}}{V^{1/3}}. \tag{105}$$

The integrating factor $f$ vanishes as $U \to 0$. $\omega/f$ is integrable along any path such that $V/N > -\beta_0/\alpha_0$, in fact, if $g(V,N)$ stays for a positive function, one has $f \sim U^{2/3} g(V,N)$ as $U \to 0^+$. If $V/N = -\beta_0/\alpha_0$, then $f \sim 3 U$ as $U \to 0^+$ and $\omega/f$ is no more integrable near $U = 0$. Notice that the entropy which corresponds to this Pfaffian form is $S = 3 (U V N)^{1/3} + \alpha_0 V + \beta_0 N \geq 0$. (N) is violated and $S$ vanishes on the submanifold $U = 0, V/N = -\beta_0/\alpha_0$. Notice that, if $S$ is not concave but simply positive, then condition (HOM) is still equivalent to (N). Notice that (HOM) is not affected by the connectedness properties of $f = 0$. 

$$p(U,V) = \begin{cases} \frac{U}{T} - \log(T) & \text{if } 0 < U < V/e^2 \\ 0 & \text{if } U = 0 \end{cases}$$

satisfies (N) but is not of class $C^1$ at $T = 0$ (the corresponding entropy is $S = V/(\log(U/V))$, which is concave on $D$ and can be continuously defined to be zero when $U = 0$). Moreover, this example shows that even the more general setting

$$S \text{ concave, } \frac{\partial f}{\partial T} \text{ finite as } T \to 0^+ \Rightarrow S \to 0^+ \text{ as } T \to 0^+$$

(which is trivial, because $\partial f/\partial U = 1 + S (\partial T/\partial U)$) does not correspond to a necessary condition for (N).

2. condition (HOM)

In order to give a necessary and sufficient condition for (N), we use the following interesting property of $\delta Q_{\text{rev}}$. We have

$$\frac{\delta Q_{\text{rev}}}{f} = \frac{dS}{S}. \tag{103}$$

Let us consider $\int_\gamma \delta Q_{\text{rev}}/f$, where $\gamma$ is a curve having final point at temperature $T$. If (N) holds, then $\int_\gamma \delta Q_{\text{rev}}/f \to -\infty$ as $T \to 0^+$. In fact, if (N) holds, whichever the path $\gamma$ one chooses, the integral of $dS/S$ diverges to $-\infty$ as $T \to 0^+$.

If, instead, $\int_\gamma \delta Q_{\text{rev}}/f \to -\infty$ as $T \to 0^+$ whichever path is chosen for approaching $T = 0$, then $S \to 0^+$ in the same limit.

Then the following theorem holds:

$$(N) \Leftrightarrow \int_\gamma \delta Q_{\text{rev}}/f \to -\infty \text{ as } T \to 0^+ \text{ whichever path is chosen in approaching } T = 0.$$

(condition (HOM) in the following)

Notice that, because of the concavity of $S$, one cannot have $\int_\gamma \delta Q_{\text{rev}}/f \to +\infty$ as $T \to 0^+$, because a non-negative and concave entropy cannot diverge (cf. sect. VII). Thus, once ensured the concavity property for $S$ (cf. [39]), one has only to check if the above integral diverges along any rectifiable curve approaching the surface $T = 0$.

Notice that, in this form, the above theorem allows to neglect the problem of the actual presence of the boundary $T = 0$ in the physical manifold. This formulation is also coherent with the fact that (N) is formulated as a limit for $T \to 0^+$.

If (N) is violated and the limit $\lim_{T \to 0^+} S$ exists, then (103) is integrable along any path approaching $T = 0$ with positive entropy (it is not integrable along any path approaching $T = 0$ with vanishing entropy). For example, let us consider the following toy-model Pfaffian form

$$\omega = dU + \left( \frac{U}{V} + \alpha_0 \frac{U^{2/3}}{(V N)^{1/3}} \right) dV + \left( \frac{U}{N} + \beta_0 \frac{U^{2/3}}{(V N)^{1/3}} \right) dN \tag{104}$$

where $\alpha_0 > 0$, $\beta_0 < 0$ are constants and the domain is restricted by $V/N \geq -\beta_0/\alpha_0$. Then one has

$$f = 3 U + \alpha_0 \frac{(U V)^{2/3}}{N^{1/3}} + \beta_0 \frac{(U N)^{2/3}}{V^{1/3}}. \tag{105}$$

The integrating factor $f$ vanishes as $U \to 0$. $\omega/f$ is integrable along any path such that $V/N > -\beta_0/\alpha_0$, in fact, if $g(V,N)$ stays for a positive function, one has $f \sim U^{2/3} g(V,N)$ as $U \to 0^+$. If $V/N = -\beta_0/\alpha_0$, then $f \sim 3 U$ as $U \to 0^+$ and $\omega/f$ is no more integrable near $U = 0$. Notice that the entropy which corresponds to this Pfaffian form is $S = 3 (U V N)^{1/3} + \alpha_0 V + \beta_0 N \geq 0$. (N) is violated and $S$ vanishes on the submanifold $U = 0, V/N = -\beta_0/\alpha_0$. Notice that, if $S$ is not concave but simply positive, then condition (HOM) is still equivalent to (N). Notice that (HOM) is not affected by the connectedness properties of $f = 0$. 

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The entropy $S$ is required to be continuous at $T = 0$. This can be obtained as follows. It is evident that the continuity of $\dot{S}$ implies the continuity of $S$. Then, one can impose conditions which allow $\dot{S}$ to be continuous at $T = 0$. Nevertheless, the continuity of $\dot{S}$ excludes, by direct inspection, the possibility to obtain $S = 0$ at $T = 0$. Thus, one has to find further conditions on $\dot{S}$ in order to allow the possibility to get a vanishing entropy at $T = 0$. Let us consider

$$
\dot{S}(\hat{B}, X^1, \ldots, X^{n+1}) = \int_{B_0}^\hat{B} d\hat{B} \frac{1}{f(\hat{B}, X^1, \ldots, X^{n+1})} + \dot{S}(\hat{B}_0, X^1, \ldots, X^{n+1}).
$$

We wish to know if the limit as $\hat{B} \to 0^+$ of $\dot{S}$ exists. A sufficient condition is the following: there exists a positive function $\phi(\hat{B})$ such that

$$
\frac{1}{f(\hat{B}, X^1, \ldots, X^{n+1})} < \phi(\hat{B}) \quad \forall \hat{B} \in (0, \hat{B}_0] \quad \text{and} \quad \forall X^1, \ldots, X^{n+1} \in C,
$$

where $C \subset \mathbb{R}^{n+1} \cap D$ is any open bounded set contained in $D$ and

$$
\lim_{\hat{B} \to 0^+} \int_{B_0}^\hat{B} d\hat{B} \phi(\hat{B}) < \infty.
$$

Then $\int_{B_0}^\hat{B} d\hat{B} 1/f$ is uniformly convergent and, being $\dot{S}$ continuous for $\hat{B} > 0$, one finds that $\dot{S}$ can be extended continuously also at $\hat{B} = 0$. This condition ensures that (N) is violated. The above condition does not leave room for $S = 0$ for some (but not all) values of $X^1, \ldots, X^{n+1} \in D$. Actually, continuity on a open bounded subset $R \subset \mathbb{R}^{n+1} \cap D$ of the allowed values for the variables $X^1, \ldots, X^{n+1}$, can be also obtained by assuming that (107) holds on $R$ and not for any open bounded set $C$ contained in $D$. In this case, $\dot{S}$ is continuous at $T = 0$ for $X^1, \ldots, X^{n+1} \in R$.

In order to obtain a condition ensuring (N) a sufficient condition is the following: there exists a positive function $\phi(\hat{B})$ such that

$$
\frac{1}{f(\hat{B}, X^1, \ldots, X^{n+1})} > \phi(\hat{B}) \quad \forall \hat{B} \in (0, \hat{B}_0] \quad \text{and} \quad \forall X^1, \ldots, X^{n+1} \in C,
$$

where again $C \subset \mathbb{R}^{n+1} \cap D$ is any open bounded set, and

$$
\lim_{\hat{B} \to 0^+} \int_{B_0}^\hat{B} d\hat{B} \phi(\hat{B}) = -\infty.
$$

Then, because the above divergence of the integral is uniform in $X^1, \ldots, X^{n+1}$, one finds that $\dot{S} = \log(S) \to -\infty$ as $T \to 0^+$, i.e. $S \to 0^+$ as $T \to 0^+$. Even in this case, one can allow the function $\phi(\hat{B})$ to be different for different subsets whose union covers all the values of the deformation parameters.

1. (N): integral criterion

We can consider

$$
\int_\Gamma \frac{\omega}{f} = \dot{S}(\hat{B}, X^1, \ldots, X^{n+1}) - \dot{S}(\hat{B}_0, X^1, \ldots, X^{n+1});
$$

due to the singularity in the integrand in $f = 0$, when one considers a path approaching $T = 0$ the integral has to be intended as improper integral. Nevertheless, according to a common use, we bypass this specification in the following. We can write

$$
\dot{S}(\hat{B}, X^1, \ldots, X^{n+1}) - \dot{S}(\hat{B}_0, X^1, \ldots, X^{n+1}) = \int_0^1 d\hat{B} \frac{a(\hat{B}, X^1, \ldots, X^{n+1})}{f(\hat{B}, X^1, \ldots, X^{n+1})}.
$$
We can see that, if \( \omega \in C^1(D \cup \partial D) \), then the above integral diverges in such a way that \( S \to 0^+ \) for \( \dot{B} \to 0^+ \). In fact, one has

\[
\hat{\xi}_i(\hat{B},X^1,\ldots,X^{n+1}) = \xi_k(\hat{B},X^1,\ldots,X^{n+1}) - \xi_k(0,X^1,\ldots,X^{n+1}) = \frac{\partial \xi_k}{\partial \hat{B}}(0,X^1,\ldots,X^{n+1}) \dot{B} + O(\dot{B}^2)
\]  

and

\[
\hat{f} = k(0,X^1,\ldots,X^{n+1}) \dot{B} + O(\dot{B}^2),
\]

where surely \( k(0,X^1,\ldots,X^{n+1}) > 0 \) because \( \hat{f} \geq 0 \). As a consequence, near \( \dot{B} = 0 \) the integrand behaves as follows:

\[
\frac{\omega}{\hat{f}} \sim \frac{1}{k \hat{B}} a d\hat{B}.
\]

Then the integral diverges as \( \log(\hat{B}) \) for \( \dot{B} \to 0^+ \). The function \( \phi(\hat{B}) \) is

\[
\phi(\hat{B}) = \sup_{(X^1,\ldots,X^{n+1}) \in C} \left( \frac{a}{k}(0,X^1,\ldots,X^{n+1}) \right) \frac{1}{\hat{B}}
\]

where \( C \) is an open bounded set contained in \( D \).

### J. inaccessibility (C) and the failure of (N)

If (N) holds, the surface \( T = 0 \) is adiabatically inaccessible along any adiabatic reversible transformation starting at \( T > 0 \), and it is a leaf of a foliation. There is no isentropic surface reaching \( T = 0 \) and the property (U) of unattainability is automatically ensured, as well as the principle of adiabatic inaccessibility (C).

The violation of (N) is instead very problematic from the point of view of (C) and of the foliation of the thermodynamic manifold. If (N) is violated, \( T = 0 \) is not a leaf and it is possible to reach \( T = 0 \) along inner (would-be) leaves \( S = \text{const} \). Actually, one does not find a foliation of the whole thermodynamic domain; if \( T = 0 \) is included in the thermodynamic manifold, one finds an “almost-foliation”, i.e. a foliation except for a zero-measure manifold, in the sense that to the proper inner foliation generated at \( T > 0 \) is joined a integral manifold \( T = 0 \) (the adiabatic boundary of the thermodynamic domain) which breaks the adiabatic inaccessibility, even if only along special paths passing through \( T = 0 \). In the spirit of the thermodynamic formalism, we agree with Einstein’s statement that the existence of such adiabatic paths is “very hurtful to one’s physical sensibilities” [23]. It is also evident that the Carnot-Nernst cycle discussed in sect. IV A is allowed, unless some discontinuity occurs or the thermodynamic formalism fails according to Planck’s objection, and that the objections against its actual performability can hold only in restricted operative conditions (from a mathematical point of view, a path contained in the surface \( T = 0 \) is different from a isentropic path at \( T > 0 \) reaching the absolute zero of the temperature). Moreover, the approach to the problem by means of \( \delta Q_{rev} \), reveals in a straightforward way aspects which other approaches cannot easily point out.

A further remark is to some extent suggested by black hole thermodynamics, where (N) is violated but states at \( T = 0 \) have \( S = 0 \). Cf. [20] for a study in terms of Pfaffian forms. In order to avoid problems occurring with the surface \( T = 0 \) if (N) is violated, one could introduce a further hypothesis. One could impose that the entropy is discontinuous at \( T = 0 \), and that

\[
\Sigma_0 < \inf_{V,X^1,\ldots,X^n} \Sigma(V,X^1,\ldots,X^n).
\]

One could then impose that \( \Sigma_0 = 0 \) for all the systems, which would allow to recover an universal behavior. Even the adiabatic inaccessibility would be restored, because the second law would inhibit to reach \( T = 0 \) adiabatically. This behavior characterizes black hole thermodynamics. Concavity would be preserved, as well as superadditivity. However this choice is arbitrary and even unsatisfactory, because a well-behaved foliation of the thermodynamic manifold is obtained by hand by means of the discontinuous entropy \( S \) just constructed. In fact, the foliation of the thermodynamic manifold, if (N) is violated, is obtained as the union of the usual foliation at \( T > 0 \) and a special leaf at \( T = 0 \). This foliation is generated by a Pfaffian form only in the inner part of the manifold.
We recall that in Gibbsian approach [47], the existence of the entropy is a postulate, because the entropy appears in an axiomatic framework. See also Refs. [48,49,17]. In a certain sense, very loosely speaking, Gibbs starts where Carathéodory leaves [50]. This can be considered the reason why in Gibbsian approach the problems which can be associated with the surface \( T = 0 \) as in the previous section appear to be less evident.

Let us assume the Gibbsian approach to thermodynamics, and write the so-called fundamental equation in the entropy representation:

\[
S = S(U, X^1, \ldots, X^{n+1})
\]

where \( X^1, \ldots, X^{n+1} \) are extensive deformation variables and \( U \) is the internal energy. \( S \) is required to be a first order positively homogeneous function and, moreover, a concave function (for mathematical details about convexity we refer to Refs. [51,52]). The former property ensures the extensivity of the entropy, the latter ensures the thermodynamic stability of the system against thermodynamic fluctuations. The second law \( \Delta S \geq 0 \) for an insulated system is also ensured.

### A. extension of \( S \) to \( T = 0 \)

Let us define

\[
I(U, X^1, \ldots, X^{n+1}) = -S(U, X^1, \ldots, X^{n+1}).
\]

In what follows, \( x \) stays for a state in the thermodynamic manifold: \( x \equiv (U, X^1, \ldots, X^{n+1}) \). The function \( I(x) \) is, by definition, a convex function and positively homogeneous function. As a consequence, its epigraph is a convex cone. This convex function \( I \) is defined on \( C \) [we change symbol for the domain, what follows holds for a generic convex function in a generic convex domain]. There is a preliminary problem. One has to define \( I(x) \) on the boundary \( \partial C \) and obtain again a convex function. This is made as follows [52]: \( I \) can be extended to the set \( F = C \cup \partial C_f \), where

\[
\partial C_f \equiv \{ y \in \partial C \mid \liminf_{x \to y} I(x) < \infty \}
\]

and

\[
I(y) \equiv \liminf_{x \to y} I(x) \quad \forall y \in \partial C_f.
\]

The above extension is convex on a convex set. In general, one cannot substitute \( \liminf_{x \to y} I(x) \) with \( \lim_{x \to y} I(x) \) because the latter may not exist [52]. Moreover, the behavior of the convex function \( I = -S \) at the boundary has to be such that

\[
\liminf_{x \to x_0} I(x) > -\infty
\]

for any \( x_0 \) belonging to the boundary of the convex domain [cf. problem F p. 95 of Ref. [52]].

In the case of \( S \), then the non-existence of the above limit can be considered unphysical. In fact, it can also mean that the entropy could approach a different value for the same state along different paths starting at the same initial point. In the latter case, its nature of state function would be jeopardized, it requires at least the existence of the limit, that is, the independence of the limit from the path chosen. On this topic, see in particular [2,3]. In any case, the definition offered by the theory of convex functions

\[
S(y) \equiv \limsup_{x \to y} S(x) \quad \forall y \in \partial C_f
\]

is a rigorous formal prescription, but it is not clear to the present author if it could be relevant to the physics at hand, if the limit does not exists.

Then, we assume that \( S \) admits a limit for each point of the boundary \( T = 0 \), thus

\[
S(y) \equiv \lim_{x \to y} S(x) \quad \forall y \in \{ T = 0 \}.
\]
Under this hypothesis, we can extend uniquely $S$ at $T = 0$. The surface $T = 0$ represents (a part of) the boundary $\partial D$ for the domain, then it belongs to the closure of the convex open set $D$. A convex set is dense in its closure. As a consequence, a continuous function $G$ defined in $D$ can be uniquely extended by continuity on the boundary $\partial D$ if (and only if), for each point $x_b \in \partial D$ the limit

$$\lim_{x \in D - x_b} G$$

exists.

It is still to be stressed that, for a non-negative concave $S$, one has to find $\lim_{T \to 0^+} S < \infty$ as a consequence of (121).

### B. attainment of the lower bound of $S$

Gibbsian approach allows us to conclude immediately that, if the upper bound $I_0$ of $I$ is attained, then it has to be attained on the boundary of the thermodynamic manifold (if a convex function $I$ should get a maximum value $I_0$ in a inner point of its convex domain, it would be actually a constant function in its domain) [52]. Then, if the lower bound $S_0$ of $S$ is attained, it is attained on the boundary of the domain of $S$. Moreover, under very simple hypotheses on the domain, the upper bound of $I$ is actually attained [51,52]. In particular, it can be attained at an extreme point of the boundary. We recall that an extreme point of a convex set is a point belonging to the boundary of the set such that it is not an inner point of any line segment contained in the set. For example, if the set is a closed rectangle, the extreme points are the four vertices; if the set is a circle, all the points of the boundary (circumference) are extreme points. But notice also that, being the thermodynamic domain a convex cone, there is no extreme point apart from the origin $0$ of the cone (which cannot be considered a physically meaningful state [39]).

Note that, given the surface $T = 0$:

$$T(U, X^1, \ldots, X^{n+1}) = 0$$

$$U = U_0(X^1, \ldots, X^{n+1})$$

then, for each point on this surface, as a consequence of the homogeneity of the entropy, it holds

$$S(\lambda U_0(X^1, \ldots, X^{n+1}), \lambda X^1, \ldots, \lambda X^{n+1}) = \lambda S(U_0(X^1, \ldots, X^{n+1}), X^1, \ldots, X^{n+1}).$$

At the same time, the intensivity (i.e., homogeneity of degree zero) of $T$ implies

$$T(\lambda U_0(X^1, \ldots, X^{n+1}), \lambda X^1, \ldots, \lambda X^{n+1}) = T(U_0(X^1, \ldots, X^{n+1}), X^1, \ldots, X^{n+1}) = 0.$$

Then, if $U_0(X^1, \ldots, X^{n+1}), X^1, \ldots, X^{n+1} \equiv X_0^a, a = 0, \ldots, n$ are the points belonging to the surface $T = 0$, the cone

$$K_0 \equiv \{ X_0^a | \lambda X_0^a \in K_0, \lambda > 0 \}$$

is contained in the surface $T = 0$ because of the intensivity of $T$. As a consequence, in case of violation of (N), one could find a system at $T = 0$ having an arbitrarily high entropy. Only if $S = 0$ at $T = 0$ this cannot happen, because $S = 0$ is a fixed point under scaling of the entropy.

### C. values of $S$ at $T = 0$ and the hypothesis of multi-branching

We have assumed a continuous $S$ at $T = 0$. From the point of view of the Landsberg's discussion about a multi-branching near $T = 0$, we have then simply to discuss the following topological problem. Is the set $Z(T)$ a connected set? In the case it is connected, then we can surely conclude that no multi-branching can occur near $T = 0$. In fact, the range of a continuous function on a connected set is a connected set, that is, the range of $S$ at $T = 0$ is a connected set contained in $\mathbb{R}$. It has to be an interval (violation of (N)) or a single point (validity of (N)). It is interesting to underline that, even if the set $Z(T)$ is not connected, (HOM) ensures the validity of (N) and viceversa (there is no possibility to find two branches like the ones in Fig. (1a), because both have to start at $S = 0, T = 0$). A possibility for getting a multi-branching is to violate the concavity at least near $T = 0$. For an interesting example see Ref. [20]. [Another possibility to get a multi-branching could be to consider a system allowing for states at $T < 0$, but in this case two distinct branches would be found on two different sides of $T = 0$].

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Consider the following toy-model:

\[ S = \gamma_0 V^{1-\alpha} U^\alpha + \delta_0 V \quad (129) \]

where \( \gamma_0 > 0, \delta_0 > 0 \) and \( 0 < \alpha < 1 \). Then

\[ T = \frac{1}{\gamma_0 \alpha} \left( \frac{U}{V} \right)^{1-\alpha} \quad (130) \]

which vanishes as \( U \to 0^+ \): \( T = 0 \iff U = 0 \). For the domain let us consider \( \mathcal{F} = \{ U \geq 0 \} \cup \{ V \geq V_0 \} \). \( I \) is maximum, that is, \( S \) is minimum, at the extreme point \((0,V_0)\), as it is evident. [Notice that in this example the domain is not a convex cone because we introduce a lower bound \( V_0 \), as it is physically reasonable in order to justify thermodynamics on a statistical mechanical ground. If one considers \( \mathcal{F} = \{ U \geq 0 \} \cup \{ V > 0 \} \), then \( \inf(S) = 0 \), which is approached at the only extreme point \((0,0)\) of the cone]. If \( \delta > 0 \), then (N) is violated and \( S \) can assume an interval of values at \( T = 0 \). If \( \delta = 0 \), then (N) is satisfied and \( I \) is maximal on the line \( U = 0 \). A special case is represented by the photon gas, where \( \alpha = 3/4 \).

This toy-model corresponds to the following behavior of \( S \) as a function of \( T \) and \( V \):

\[ S(T,V) = (\epsilon_0 T^{\frac{\alpha}{1-\alpha}} + \delta_0) V \quad (131) \]

which, for \( \delta_0 \neq 0 \), violates (N). It is useful to pass to the energy representation

\[ U = \left( \frac{S - \delta_0 V}{\gamma_0} \right)^{\frac{1}{\alpha}} V^{\frac{\alpha-1}{\alpha}}. \quad (132) \]

The domain is \( \mathcal{G} = \{ V_0 \leq V \leq S/\delta_0 \} \). The \( T = 0 \) surface corresponds to \( V = S/\delta_0 \). We have

\[ T = \frac{1}{\alpha} \frac{1}{\gamma_0} V^{\frac{\alpha-1}{\alpha}} (S - \delta_0 V)^{\frac{1}{\alpha}-1} \quad (133) \]

the pressure is

\[ p = \frac{1}{\alpha} \left( \frac{1}{\gamma_0} \right)^{\frac{1}{\alpha}} (S - \delta_0 V)^{\frac{1}{\alpha}-1} V^{-\frac{1}{\alpha}} (S (1-\alpha) + V \alpha \delta_0). \quad (134) \]

The isentropic \( S = S_0 \) has equation

\[ U(V) = \left( \frac{S_0 - \delta_0 V}{\gamma_0} \right)^{\frac{1}{\alpha}} V^{\frac{\alpha-1}{\alpha}} \quad (135) \]

and reaches \( T = 0 \) when \( V = S_0/\delta_0 \) during an adiabatic expansion. It is easy to see that it is tangent to the \( T = 0 \) surface. The adiabatic expansion has to stop there, because of the structure of the domain. One can wonder if any physical reason for such a stopping exists. It is useful to come back to Landsberg’s suggestion about a possible vanishing of the adiabatic compressibility:

\[ K_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S. \quad (136) \]

In our case, we get

\[ K_S = \alpha^2 \frac{1}{\gamma_0} \frac{1}{1-\alpha} \frac{1}{S^2} V^{\frac{\alpha}{\alpha-1}} (S - \delta_0 V)^{\frac{2\alpha-1}{\alpha}} \quad (137) \]

and three cases occur: when \( 1/2 < \alpha < 1 \) then \( K_S \to 0 \) as \( T \to 0^+ \), in such a way that the elastic constants of the system diverge in that limit, forbidding any further expansion (Landsberg’s behavior); when \( 0 < \alpha < 1/2 \) then \( K_S \to \infty \) as \( T \to 0^+ \), the elastic constants vanish and the behavior of the system is pathologic (the system appears to be “totally deformable” in that limit); when \( \alpha = 1/2 \) then \( K_S \to \gamma_0^2 V^2/(2 S^2) \) which is in any case finite (\( S \) is surely
E. further properties

Another point that can be underlined is the following. Let us assume to extend the convex function \( I = -S \) to all of \( \mathbb{R}^n \), by defining \( I = +\infty \) outside its domain \( \text{dom} \, I \). Then, replace this function with its closure. This is the same procedure which is prescribed in Ref. [53] for the internal energy \( U \). Then \( I \) is a closed proper convex function which is \textit{essentially smooth}, that is, \(|\nabla I| \to \infty\) for any subsequence converging to a boundary point. In fact, in the gradient of \( I \) appears the factor \( 1/T \) which diverges as the boundary \( T = 0 \) is approached. This allows to obtain in thermodynamics a convex function of Legendre type, which is relevant for the discussion of Legendre transformations in thermodynamics. The difference of the entropy representation with respect to the energy representation is evident from this point of view. In fact, the opposite conclusion appears in Ref. [53] for the energy representation: no Legendre type function exists in thermodynamics. But we think, from the discussion of the previous section, that the entropy representation is more fundamental with respect to the energy representation at least for the discussion of the boundary \( T = 0 \).

Summarizing our analysis in Gibbs framework:

\( g1 \) if \( S \geq 0 \), then \( S = 0 \) can be attained at a point of the boundary of the domain;
\( g2 \) it could be that \( S > 0 \) at other points on the surface \( T = 0 \). Then, homogeneity implies that, by scaling, a system with an arbitrarily high zero temperature entropy could be obtained;
\( g3 \) models exist where the violation of (N) does not imply the attainability of \( T = 0 \) and the violation of \( \Delta S = 0 \) for adiabatic reversible transformations (states at \( T = 0 \) are not available and so no such violation can occur at \( T = 0 \)). But these systems display a non-universal behavior (i.e., a behavior which does not appear in other models).

VIII. CONCLUSIONS

We have discussed the status of third law of thermodynamics and we have given an heuristic argument in favor of the entropic version of the third law. Then, we have analyzed the law both in Carathéodory’s approach and in Gibbs’ approach to thermodynamics.

In particular, Carathéodory’s approach shows that for \( T > 0 \) the thermodynamic manifold can be foliated into leaves which correspond to isentropic surfaces. The only hypothesis is that the Pfaffian form \( \delta Q_{\text{rev}} \) is integrable and \( C^1 \) in the inner part \( (T > 0) \) of the thermodynamic manifold. At the boundary \( T = 0 \), which is assumed to be an integral manifold of the Pfaffian form \( \delta Q_{\text{rev}} \), the aforementioned Pfaffian form is allowed to be also only continuous. The special integral manifold \( T = 0 \) is problematic from a physical point of view, because it can also be intersected by the inner (would-be) leaves \( S = \text{const} \). In the latter case, (N) is violated and one obtains an almost-foliation of the thermodynamic manifold, where the inaccessibility property fails, even if only along special adiabatic paths which pass through the surface \( T = 0 \). For an entropy which is continuous also at \( T = 0 \), (N) holds if and only if \( T = 0 \) is a leaf. This is a remarkable result, the validity of (N) is strongly related to the possibility to obtain a foliation for the whole thermodynamic manifold, including \( T = 0 \). We have shown that, if the Pfaffian form is \( C^1 \) everywhere, then (N) is preserved. Physical assumptions and mathematical conditions have been discussed.

In another paper [19], further conditions leading to the third law are discussed.

We add herein some notes about the conditions ensuring (N) in quasi-homogeneous thermodynamics introduced in [54]. Also in the quasi-homogeneous case (N) holds iff \( \lim_{T \to 0^+} S = 0 \). The analysis of sects. VIF and VIG hold with obvious changes; moreover, condition (HOM) holds unaltered, and, if the Pfaffian form \( \omega \) is \( C^1 \) everywhere, then (N) holds (this can be shown by using a criterion analogous to the one appearing in (VI11)).
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