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2003 J. Phys. A: Math. Gen. 36 8165

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Notes on the third law of thermodynamics: I

F Belgiorno

Dipartimento di Fisica–Sezione Teorica, Università degli Studi di Milano, Via Celoria 16,
20133 Milano, Italy

E-mail: belgiorno@mi.infn.it

Received 16 October 2002, in final form 3 June 2003

Published 16 July 2003

Online at stacks.iop.org/JPhysA/36/8165

Abstract

We analyse 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 δQ_{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 S has to be attained at the boundary of the convex set where S is defined.

PACS number: 05.70.–a

1. Introduction

We re-analyse 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 δQ_{rev} is expressed in terms of independent extensive variables. One finds that $T = 0$, as an

integral manifold of δQ_{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 appears 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 analysed. Carathéodory's and Gibbs' approaches together allow us to better define the problem of the third law.

The plan of the paper is the following. In section 2, a discussion of the third law is given. In section 3, 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 interpreted in a natural way as a continuity boundary condition, in the sense that it corresponds to the natural extension of thermodynamics to the states at $T = 0$. In section 4, we remark that Planck's restatement of the third law is not conventional but mandatory for homogeneous systems. In section 5, it is shown that, in the framework of the Carathéodory approach, (N) is equivalent to ensuring that the surface $T = 0$ is a leaf of the thermodynamic foliation associated with the Pfaffian form δQ_{rev} . The isentropic surfaces cannot intersect the $T = 0$ surface, because no common point between distinct leaves of the foliation determined by δQ_{rev} is allowed. Some problems arising when (N) is violated are discussed, and it is recalled that a singular behaviour occurs if the entropic version (N) fails. In section 6, a Gibbsian approach to the problem is sketched. We show that the entropy can reach its minimum value (if any) only at the boundary $T = 0$ of its domain.

2. The third law

The third law of thermodynamics has been formulated in two ways. The original formulation of Nernst concerns the behaviour 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, \dots, x^n , the entropy difference $\Delta_T S \equiv S(T, x^1, \dots, x^n) - S(T, \bar{x}^1, \dots, \bar{x}^n)$ goes to zero as $T \rightarrow 0^+$

$$\lim_{T \rightarrow 0^+} \Delta_T S = 0 \quad (1)$$

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

$$\lim_{T \rightarrow 0^+} S = 0 \quad (2)$$

and it is trivially mandatory for homogeneous systems (cf section 4).

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 has been remarked in Landsberg's studies, which are in many respects corner stones of this topic and in general of the third law of thermodynamics [1–3]. A detailed analysis shows that in standard thermodynamics unattainability (U) implies (N) if the following conditions are satisfied [1, 3]: (a) the stability condition $(\partial S / \partial T)_{x^1, \dots, x^n} > 0$ is satisfied for any transformation such that the external parameters (or deformation coordinates) x^1, \dots, x^n are kept fixed; (b) there are no

multiple branches in thermodynamic configuration space; (c) there is no discontinuity in thermodynamic properties of the system near absolute zero.

A full implication $(N) \Rightarrow (U)$ is possible in the case where unattainability means the absence of quasi-static adiabatic transformations reaching $T = 0$ (as in the standard treatment). Actually, a more general notion of unattainability can be assumed: ‘zero temperature states do not occur in the specification of attainable states of systems’. This is almost literally the (U4) principle as in [1, 2]. (U4) states that no process allows us to reach states at $T = 0$, even as transient non-equilibrium states. In general, (U4) allows a de-linking of (U) and (N) and implies that $(N) \not\Rightarrow (U)$ and $(U) \not\Rightarrow (N)$ [1, 2]. 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 some process allows us to reach $T = 0$ [1, 2]. The reader is referred to the aforementioned studies for details. We premise that our discussion often refers to these papers. About the inequivalence between (U) and (N), see also [4, 5]. We also recall that the standard approach to Nernst’s theorem involves heat capacities [6, 7] (see also [8]).

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 [9, 10], whereas in [11] models displaying a violation of (1) are given. Moreover, it is commonly stated that a violation of (N) occurs if the ground state is degenerate. As far as the limit as $T \rightarrow 0^+$ is concerned, one has to distinguish between finite-size systems and bulk systems. Griffiths shows that the behaviour of bulk systems near absolute zero, in measurements, is determined by the contribution of the excitable low-lying energy states; the contribution of the ground state, at reachable low temperatures, is instead irrelevant. In statistical mechanics, the ground-state degeneracy for bulk systems does not play a straightforward role in determining the behaviour as absolute zero is approached, and examples exist where the ground state is not degenerate but the limit $S \rightarrow 0^+$ is not implemented [9]. However, a role for the degeneracy of the ground state can be suitably resorted as in [10]. 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 absolute zero can be related to a maximally degenerate ground state by means of a variational criterion [10]. We limit ourselves to referring the reader to [12] for a further approach to the problem of the third law by means of the concept of dynamical entropy and to [13] for another interesting point of view concerning the problem of the third law in the presence of ground-state degeneracy.

The validity of thermodynamics for finite-size systems if T is sufficiently near absolute zero has been questioned. A corner-stone of this topic is represented by Planck’s objection (see [14] 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 it impossible even to define an entropy. The same problem is analysed in [15] where the breakdown of thermodynamics near 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 [15] near absolute zero it is no longer possible to neglect statistical fluctuations in the calculation of thermodynamic quantities such as T , S because they are of the same order as the ‘standard’ leading terms¹. 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,

¹ The example of [15] 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 $T \sim 10^{-5} \text{ K}$.

then the formal success of the thermodynamic approach follows. For more details see [15] (see also [16]). We do not discuss this topic further in this paper.

In [6, 15] it is proposed, in agreement also with the general axiomatic approach of [1, 2], 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 absolute zero. To some extent, the application of the thermodynamic equations to 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 [6]. In section 3, we come back to this topic and give an interpretation of the Nernst heat theorem as a ‘continuity’ boundary condition for thermodynamics at $T = 0$. Moreover, 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 reaching a particular state at $T = 0$) of the thermodynamic variables at ‘inner points’ of the thermodynamic configuration space and this is proposed as the only satisfactory approach to the definition of thermodynamic variables at absolute zero [1, 2].

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 principles [17], in the (U) version simply does not allow to get $T = 0$, whereas in the (N) version it also implies 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 $T_1 \rightarrow 0^+$ (see [18]). For an extensive discussion of the third law, see also [19–25]. See also the recent discussions in [26–30].

3. 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 a 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 [3], 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, $\Delta S = 0$ for adiabatic reversible transformations at $T > 0$. Then, let us consider ideally which behaviour is natural to postulate for thermodynamics at $T = 0$. Along the $T = 0$ isotherm any reversible transformation is adiabatic. From the point of view of thermodynamic formalism, a discontinuity with respect to the natural identification between adiabats and isentropes arises if the states at $T = 0$ are not assumed to be isentropic. From our point of view, the (N) version of the Nernst heat theorem appears to be associated with a ‘continuity boundary condition’ for thermodynamics at $T = 0$. Continuity means that the entropy is continuous also at the boundary $T = 0$ and that the identification between isentropic transformations and adiabatic reversible transformations holds also at $T = 0$. In fact, by continuity, it is natural, from the point of view of classical thermodynamics, to postulate that states at $T = 0$ are isentropic and then in the T – S plane the $T = 0$ line reduces to a single point ($T = 0, S = \text{const}$). But, in order to match continuously the property that any isothermal

reversible transformation $\gamma_{T=0}$ at $T = 0$ is isentropic, i.e. $\Delta S = 0 \forall \gamma_{T=0}$, one has to require that along the isothermal surfaces the entropy variation becomes smaller and smaller, that is, $\Delta_T S \equiv S(T, x^1, \dots, x^n) - S(T, \bar{x}^1, \dots, \bar{x}^n)$ at fixed external parameters has to converge to zero as $T \rightarrow 0^+$. The underlying hypotheses are:

- (η_0) $T = 0$ belongs to the equilibrium thermodynamic phase space;
- (η_1) it is possible ideally to conceive transformations at $T = 0$;
- (η_2) transformations at $T = 0$ are adiabatic reversible;
- (η_3) transformations at $T = 0$ are isentropic;
- (η_4) there is a continuous match between states at $T = 0$ and states at $T > 0$.

Actually, (η_4) could even summarize all the hypotheses above, in the sense that a violation of at least one hypothesis (η_0), (η_1), (η_2) and (η_3) would imply a discontinuity in thermodynamics between zero-temperature states and non-zero ones. For a discussion of (η_1), see appendix A.

A final comment is that it is often stated that the third principle is not as fundamental as the first and the second ones and that it is not related to any new potential in thermodynamics, whereas the first law is associated with the internal energy function and the second law with the entropy [4]. On this side of the topic, the third law prescribes the behaviour of the zero-temperature part of the entropy $\lim_{T \rightarrow 0^+} S(T, x^1, \dots, x^n) = S(0, x^1, \dots, x^n) \equiv \Sigma(x^1, \dots, x^n)$ and fixes its value at zero. We shall show that

The third law of thermodynamics (Planck's restatement) corresponds to a regularity condition of the Pfaffian equation $\delta Q_{\text{rev}} = 0$ at 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.

4. 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, $S \rightarrow 0^+$ as $T \rightarrow 0^+$, because the constant S_0 (entropy at $T = 0$), which does not depend on the thermodynamic parameters, does not affect any physical measurement [31]. According to some authoritative experts in the field of thermodynamics, this corresponds to a sufficient condition for implementing (N), not a necessary one [18, 20, 32–34]. We discuss the problem *in the framework of the thermodynamics of homogeneous systems*. We first point out that the density of the thermodynamic domain in its closure, in particular near its boundary $T = 0$ (see also the following sections), is a topological condition which allows us to extend uniquely by continuity to $T = 0$ a continuous function h such that $\lim_{T \rightarrow 0^+} h$ exists. This allows us to define S at $T = 0$ as the limit of S as $T \rightarrow 0^+$, in agreement with the discussion in [1, 3] and with (N), and does not allow that an unnatural eliminable discontinuity $S(0, x^1, \dots, x^{n+1}) \neq \lim_{T \rightarrow 0^+} S(T, x^1, \dots, x^{n+1})$ when the latter limit exists. Then we prove a result which is valid in general:

Result 1. *A necessary condition for (N) to hold is that $S(T, x^1, \dots, x^{n+1})$ is continuous in the limit as $T \rightarrow 0^+$, whichever limit state $(0, x^1, \dots, x^{n+1})$ is considered at $T = 0$.*

Proof. Let us define $X \equiv x^1, \dots, x^{n+1}$ and let us assume that S is not continuous in $(0, X_0)$. If this discontinuity is not simply an eliminable one, which is excluded, then there exist two

different sequences $\{T_k^{(i)}, X_k^{(i)}\}$, with $i = 1, 2$, such that $(T_k^{(i)}, X_k^{(i)}) \rightarrow (0, X_0)$ as $k \rightarrow \infty$ and, moreover, such that

$$\lim_{k \rightarrow \infty} S(T_k^{(1)}, X_k^{(1)}) \neq \lim_{k \rightarrow \infty} S(T_k^{(2)}, X_k^{(2)}). \quad (3)$$

(N) is badly violated (see also section 7). \square

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 be included in the set of what we called deformation parameters². The aforementioned independence is a consequence of result 2 below for an homogeneous system.

The choice $S_0 = 0$ for homogeneous systems is not simply a convention, which does not amount to a real loss of generality, because measurements leave the constant undetermined³; it is also a necessity (if the third law holds), in fact it holds

Result 2. *Let us consider an homogeneous system which satisfies (N). Then (N) holds in Planck's restatement, i.e., $\lim_{T \rightarrow 0^+} S = 0$.*

Proof. For what follows, it is sufficient that S is a continuous function. If one considers independent variables $T, x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1}$, where y^i are extensive variables for $i = k+1, \dots, n+1$ and T, x^1, \dots, x^k are intensive variables, then $S(T, x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1})$ is a homogeneous function of degree one in the extensive variables (see, e.g., [20]). One can also say that S is a quasi-homogeneous function of degree one and weights which are 0 for the first $k+1$ intensive variables and 1 for the remaining extensive variables, i.e. it satisfies $S(T, x^1, \dots, x^k, \lambda y^{k+1}, \dots, \lambda y^{n+1}) = \lambda S(T, x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1})$ [36].

If (N) is satisfied, then

$$\lim_{T \rightarrow 0^+} S(T, x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1}) = S_0 \quad (4)$$

for any choice of $x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1}$. Because of the aforementioned quasi-homogeneity, for any real $\lambda > 0$ one has

$$\lim_{T \rightarrow 0^+} S(T, x^1, \dots, x^k, \lambda y^{k+1}, \dots, \lambda y^{n+1}) = \lambda S_0 \quad (5)$$

which is consistent with the independence of the limit from $x^1, \dots, x^k, y^{k+1}, \dots, y^{n+1}$ only for $S_0 = 0$. \square

Summarizing:

Planck's restatement of the third law is mandatory in homogeneous thermodynamics.

5. Carathéodory's approach and (N)

In Carathéodory's approach [37], the infinitesimal heat exchanged reversibly δQ_{rev} , defined on a open simply connected domain \mathcal{D} , is a Pfaffian form, i.e. a one-form ω , whose integrability has to be ensured in order to define an entropy function, see, e.g., [17, 38–41]. This approach appears to be very clarifying with respect to the problem represented by the special surface $T = 0$. In the following, we use $\omega \equiv \delta Q_{\text{rev}}$.

² This choice can be opinable in light of a rigorous axiomatic approach [35], 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.

³ In order to understand this point, it is important to underline that the constant S_0 has actually no operative meaning, in the sense that thermodynamic measurements (and extrapolations for the limit $T \rightarrow 0^+$) are relative to the integral of C/T . So, in line of principle, it can be put equal to 0 without affecting thermodynamic measurements.

5.1. Foliation in thermodynamics

Carathéodory's *principle of adiabatic inaccessibility* is usually stated for the case where \mathcal{D} has no boundary, that is, $\partial\mathcal{D} = \emptyset$ [40, 41]. It can be formulated as follows:

(C): *each neighbourhood of any state x_0 belonging to the domain \mathcal{D} contains states which are inaccessible from x_0 along solutions of $\omega = 0$.*

This principle ensures that the Pfaffian form ω 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 theory⁴. The integrability condition

$$\omega \wedge d\omega = 0 \quad (6)$$

has to be imposed in the interior of the domain of the differential form ω , where ω is required to be at least C^1 . These properties ensure that the Frobenius theorem can be applied and one obtains a foliation in the inner part of the manifold. 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 ω [42]. 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 ω at 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 δQ_{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 a 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 $T = 0$, which is an integral submanifold of ω , is a leaf itself. In the following subsections, we analyse the above problem in detail.

5.2. Domain \mathcal{D}

Let \mathcal{D} be the thermodynamic manifold whose independent coordinates are the extensive variables U, V, X^1, \dots, X^n ; the variables V, X^1, \dots, 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 $(\lambda U, \lambda V, \lambda X^1, \dots, \lambda X^n)$ belongs to \mathcal{D} for each real positive λ , 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 [43]. One can also relax to some extent the latter condition (e.g., a positive lower bound on V, N should be introduced on physical grounds, they cannot be arbitrarily near the zero value or statistical fluctuations would not allow us to define a meaningful thermodynamic state (cf [43])).

5.3. 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

⁴ The author is indebted to Lawrence Conlon for an enlightening e-mail about the problem of the Frobenius theorem for manifolds with boundary.

thermodynamic manifold. One can write

$$\delta Q_{\text{rev}} = dU + p dV - \sum_i \xi_i dX^i \quad (7)$$

where (U, V, X^1, \dots, X^n) are extensive variables. The integrability of δQ_{rev} ensures that

$$\delta Q_{\text{rev}} = T dS. \quad (8)$$

We assume that δQ_{rev} is an homogeneous Pfaffian form of degree one. This means that the vector field

$$Y \equiv U \frac{\partial}{\partial U} + V \frac{\partial}{\partial V} + \sum_i X^i \frac{\partial}{\partial X^i} \quad (9)$$

is a symmetry for δQ_{rev} [44–46], in the sense that

$$L_Y \delta Q_{\text{rev}} = \delta Q_{\text{rev}} \quad (10)$$

where L_Y is the associated Lie derivative. It can be shown that, in the homogeneous case [43], an integrating factor for (7) exists and it is given by

$$f \equiv i_Y \delta Q_{\text{rev}} = \delta Q_{\text{rev}}(Y) = U + pV - \sum_i \xi_i X^i. \quad (11)$$

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 δQ_{rev} (cf [45]). 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 [43]. One finds

$$\delta Q_{\text{rev}} = f d\hat{S} \quad (12)$$

and it can be shown in general that, for any homogeneous integrable Pfaffian form, ω/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 [43] (see also [46] for a general proof). This function H is actually the entropy S , as can be straightforwardly deduced also by direct comparison with the extensivity property of S

$$S = \frac{1}{T}U + \frac{p}{T}V - \sum_i \frac{\xi_i}{T}X^i \quad (13)$$

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

$$d\hat{S} = \frac{\omega}{f} = \frac{dS}{S} \quad (14)$$

which implies

$$S = S_0 \exp\left(\int_{\Gamma} \frac{\omega}{f}\right) \quad (15)$$

where Γ indicates a path between a reference state $U_0, V_0, X_0^1, \dots, X_0^n$ and the state U, V, X^1, \dots, X^n . We require that the thermodynamic foliation is described everywhere in \mathcal{D} by the leaves $\hat{S} = \text{const}$, which means that \hat{S} has to be defined everywhere in the thermodynamic manifold (except maybe at the boundary $f = 0$) [43]. The only problems can occur where $f = 0$. Moreover, one also assumes that to each level set $S = \text{const}$ corresponds a unique leaf (which means that each isentropic surface is path-connected, as it is natural to assume).

5.4. Zeros of the integrating factor and the domain

Let us define the set

$$Z(f) \equiv \{(U, V, X^1, \dots, X^n) \mid f(U, V, X^1, \dots, X^n) = 0\}. \quad (16)$$

$Z(f)$ is the set of the zeros of f . We define also

$$Z(T) \equiv \{(U, V, X^1, \dots, X^n) \mid T(U, V, X^1, \dots, X^n) = 0\} \quad (17)$$

and

$$Z(S) \equiv \{(U, V, X^1, \dots, X^n) \mid S(U, V, X^1, \dots, X^n) = 0\}. \quad (18)$$

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

5.4.1. $Z(T)$. The surface $T = 0$ is usually excluded from the thermodynamic domain (see e.g., [35, 48, 49]). From the point of view of the approach involving extensive variables, it has to be discussed if $Z(T)$ is empty or not (it is surely non-empty in the black-hole case (see also [50])). In the former case, it should be discussed if there is a lowest temperature [1] (maybe different for each system) and what this implies for the physics. A different lowest temperature for each system is not a viable hypothesis, because one could put in thermal contact a system at its own lowest temperature with another system at a lower temperature and should see an heat flux from the former to the latter, and a decrease in temperature of the former. Thus, a lowest temperature should be allowed to be the same for all systems. Moreover, from an experimental point of view there is no apparent limit to the possibility of approaching $T = 0$. From a theoretical point of view, there is actually no physical hindrance to consider $T = 0$ as a possible value. From a mathematical point of view, the Pfaffian form δQ_{rev} vanishes at $T = 0$ but it is non-singular. A singularity of a Pfaffian form $\omega \equiv \sum_i a_i(x) dx^i$ is defined as the set where $a_i(x) = 0 \forall i$, i.e., where all the coefficients of the Pfaffian form vanish. But in the thermodynamic case, no singularity is allowed, because of the coefficient of the internal energy term, which is in any case one. Thus, no mathematical hindrance to consider $T = 0$ in the thermodynamic domain appears. The singularity appears only when T is used as independent variable, and it is due to the fact that the change of variable $U \mapsto T$ is a diffeomorphism only for $T > 0$. See also the following subsection. This topic is also discussed in [51].

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

$$T(U, V, X^1, \dots, X^n) = 0 \quad (19)$$

is required to be implemented for any value of V, X^1, \dots, 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 were 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 subsection 5.5).

5.4.2. $Z(S)$. 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 shown in section 6. $S = 0$ can moreover be attained only at 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 of allowing the system only to absorb heat along any path γ_z starting from z in a neighbourhood W_z of z . If $C_\gamma(T)$ is the heat capacity along a path γ which does not contain isothermal sub-paths, one has that

$$S(y) = \int_{T_z}^{T_y} \frac{dT}{T} C_{\gamma_z}(T) \quad (20)$$

should be positive for any state y non-isentropic 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 ΔS should be positive in a neighbourhood of z , $S = 0$ being 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 the Clausius formulation. Then, no possibility to approximate such a thermal contact by means of a reversible transformation exists, and this behaviour 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 formulae of thermodynamics, one has for all T and for all x^1, \dots, x^{n+1}

$$S(T, x^1, \dots, x^{n+1}) = S(0, x^1, \dots, x^{n+1}) + \int_0^T \frac{dz}{z} C_{x^1, \dots, x^{n+1}}(z) > 0 \quad (21)$$

x^1, \dots, x^{n+1} are deformation parameters (they could also be in part intensive); because of the concavity condition $C_{x^1, \dots, x^{n+1}}(T) > 0$ the entropy can vanish only for $T = 0$. A further discussion is found in subsection 5.5.

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

$$Z(S) \subseteq Z(T). \quad (22)$$

The two sets coincide if (N) holds, otherwise $Z(S) \subset Z(T)$ and $Z(S) = \emptyset$ is also allowed.

Then we get the following equality:

$$Z(f) = Z(T). \quad (23)$$

If one considers a concave entropy which can also be 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 [47]

$$S(U, V, N) = N \left[\frac{5}{2} + \log \left(\frac{U^{3/2} V}{N^{5/2} (3\pi)^{3/2}} \right) \right] \quad (24)$$

the corresponding Pfaffian form is

$$\omega = dU + \frac{2}{3} \frac{U}{V} dV + \frac{2}{3} \frac{U}{N} \log \left(\frac{U^{3/2} V}{N^{5/2} (3\pi)^{3/2}} \right) dN \quad (25)$$

and one has

$$T = \frac{2}{3} \frac{U}{N} \quad (26)$$

and

$$f = \frac{2}{3} U \left[\frac{5}{2} + \log \left(\frac{U^{3/2} V}{N^{5/2} (3\pi)^{3/2}} \right) \right]. \quad (27)$$

In this case one has

$$Z(T) = \{U = 0\} \quad (28)$$

and

$$Z(S) = \left\{ (U, V, N) \left| \frac{U^{3/2} V}{N^{5/2}} \frac{1}{(3\pi)^{3/2}} = \exp\left(-\frac{S}{2}\right) \right. \right\}. \quad (29)$$

Then $Z(f) \supset Z(T)$ and f vanishes before $U = 0$ is reached.

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 $\mathcal{D} \cup \partial\mathcal{D}$, in fact $f = 0$ defines a C^1 hypersurface contained in the domain. This submanifold could be trivially an hyperplane $U = U_0 = \text{const}$, or a non-trivial hypersurface $U = b(U, V, X^1, \dots, X^n)$. A further discussion is found in subsection 5.5 and in subsection 6.3.

5.5. Boundary revisited

In thermodynamics, as discussed in section 5.4, 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:

$$U = b(X^1, \dots, X^{n+1}); \quad (30)$$

in the following, we replace for simplicity the set of independent extensive variables V, X^1, \dots, X^n with the set X^1, \dots, X^{n+1} . By assuming that the function b is bounded from below, one can figure that (30) corresponds to the equation for the ground-state energy of the system as a function of the deformation parameters. b is a function which is homogeneous of degree one with respect to (X^1, \dots, X^{n+1}) :

$$b(\lambda X^1, \dots, \lambda X^{n+1}) = \lambda b(X^1, \dots, X^{n+1}). \quad (31)$$

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

$$T(U, X^1, \dots, X^{n+1}) = \int_{U_0}^U dU \frac{\partial T}{\partial U}(U, X^1, \dots, X^{n+1}) \quad (32)$$

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

$$\text{epi}(b) \equiv \{(U, X^1, \dots, X^{n+1}) \mid (X^1, \dots, X^{n+1}) \in \mathcal{K}_b, U \geq b\}. \quad (33)$$

This set is the so-called epigraph of the function b . If the function $b(X^1, \dots, X^{n+1})$ is required to be convex, then it is defined in the convex cone \mathcal{K}_b , and its epigraph $\text{epi}(b)$ is a convex cone (the epigraph of a homogeneous b is a cone). Then, the domain can be chosen to be

$$\mathcal{D} \cup \partial\mathcal{D} = \text{epi}(b). \quad (34)$$

One can also assume that $\mathcal{D} \cup \partial\mathcal{D}$ is a convex cone of the form (33) such that $\mathcal{K}_b \equiv I_{X^1} \times \dots \times I_{X^{n+1}}$, where $I_{X^1}, \dots, I_{X^{n+1}}$ are intervals ($\overline{\mathbb{R}}_+, \overline{\mathbb{R}}_-$ or \mathbb{R}). We can find coordinates (B, X^1, \dots, X^{n+1}) such that the boundary $T = 0$ coincides with $B = 0$. In fact, we can simply define

$$B \equiv U - b(X^1, \dots, X^{n+1}). \quad (35)$$

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

$$U = B + b(X^1, \dots, X^{n+1}). \quad (36)$$

As a consequence, one gets

$$\bar{f} \equiv f(B, X^1, \dots, X^{n+1}) = B + b(X^1, \dots, X^{n+1}) - \sum_k \xi_k X^k \quad (37)$$

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

$$0 = b(X^1, \dots, X^{n+1}) - \sum_k \xi_k(0, X^1, \dots, X^{n+1}) X^k \quad (38)$$

$$\Leftrightarrow \frac{\partial b}{\partial X^k} = \xi_k(0, X^1, \dots, X^{n+1}) \quad \forall k. \quad (39)$$

Note that, by defining for all $i = 1, \dots, n+1$

$$\tilde{\xi}_i(B, X^1, \dots, X^{n+1}) \equiv \xi_i(B, X^1, \dots, X^{n+1}) - \frac{\partial U}{\partial X^i}(B, X^1, \dots, X^{n+1}) \quad (40)$$

one finds

$$\omega = dB - \sum_i \tilde{\xi}_i(B, X^1, \dots, X^{n+1}) dX^i \quad (41)$$

and it holds $\tilde{\xi}_i(B=0, X^1, \dots, X^{n+1}) = 0$ for all $i = 1, \dots, n+1$, because of the assumption for $f = 0$ to be an integral hypersurface for ω . Moreover, note that, under this assumption about the domain $\mathcal{D} \cup \partial\mathcal{D}$, one obtains that $Z(S) \subseteq Z(T)$ necessarily. In fact, one can write for an everywhere continuous entropy

$$S(B, X^1, \dots, X^{n+1}) = S(0, X^1, \dots, X^{n+1}) + \int_0^B dY \frac{1}{T(Y, X^1, \dots, X^{n+1})} \quad (42)$$

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

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

$$\frac{\partial S}{\partial B} = \frac{1}{T(B, X^1, \dots, X^{n+1})} \quad (43)$$

$$\frac{\partial S}{\partial X^i} = -\frac{\tilde{\xi}_i(B, X^1, \dots, X^{n+1})}{T(B, X^1, \dots, X^{n+1})} \quad \forall i = 1, \dots, n+1. \quad (44)$$

5.5.1. A further setting for the boundary. Let us consider in general the boundary $f = 0$ as a boundary of a differentiable manifold. Then the manifold is locally homeomorphic to $H^{n+2} \equiv \{(y^0, \dots, y^{n+1}) \in \mathbb{R}^{n+2} \mid y^0 \geq 0\}$ and one can find a local coordinate system y^0, \dots, y^{n+1} such that $y^0 \geq 0$ and the boundary is identified by $y^0 = 0$. An atlas of such charts allows us to cover the whole boundary, with standard treatment for the transition functions allowing to pass from a chart to another in the regions where charts overlap. There is a regular local map $U, X^1, \dots, X^{n+1} \mapsto y^0, y^1, \dots, y^{n+1}$ such that locally

$$\omega = \sum_{i=0}^{n+1} a_i(y^0, y^1, \dots, y^{n+1}) dy^i \quad (45)$$

with straightforward relations between the coefficients a_i in these coordinates and the ‘thermodynamic’ coefficients above. In order that $y^0 = 0$ is an integral hypersurface, one has to require that $a_i(y^0 = 0, y^1, \dots, y^{n+1}) = 0$ for all $i = 1, \dots, n+1$ and that

$a_0(y^0 = 0, y^1, \dots, y^{n+1}) \neq 0$ because ω is non-singular. One may also be allowed to introduce a regular transformation $U \mapsto \hat{B}$ such that the boundary coincides with $\hat{B} = 0$ (as e.g., when the domain is as in (34)). Then one can find

$$\omega = \frac{\partial U}{\partial \hat{B}} d\hat{B} - \sum_i \hat{\xi}_i(\hat{B}, X^1, \dots, X^{n+1}) dX^i \quad (46)$$

where one has $\hat{\xi}_i(\hat{B} = 0, X^1, \dots, X^{n+1}) = 0$ for all $i = 1, \dots, n+1$.

Note that, because of the properties of the Pfaffian form ω , the absolute temperature T cannot be used as a good coordinate for the boundary, in fact $\partial U / \partial T \rightarrow 0$ as $T \rightarrow 0^+$ 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 ω 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 [51]).

5.6. 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^i stays for any extensive variable different from U and ξ_i for the corresponding intensive variable)

$$\frac{\partial U}{\partial X^i}(X^1, \dots, X^{n+1}) = \xi_i(U, X^1, \dots, X^{n+1}) \quad \text{for } i = 1, \dots, n+1. \quad (47)$$

One can also assign an initial condition

$$U(X_0^1, \dots, X_0^{n+1}) = U_0 \quad (48)$$

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 at the $T = 0$ boundary allows solutions which lie in $T = 0$. Let us consider the following differential equation which describes isentropic curves in the special coordinates adapted to the boundary introduced in subsection 5.5:

$$\frac{dB}{d\tau} = \sum_i \tilde{\xi}_i(B(\tau), X^1(\tau), \dots, X^{n+1}(\tau)) \frac{dX^i}{d\tau}. \quad (49)$$

This equation can be easily obtained from (47) and $\tau \in [0, 1]$. Let us consider at least piecewise C^1 functions $X^1(\tau), \dots, X^{n+1}(\tau)$ for $\tau \in [0, 1]$. These functions are arbitrarily assigned. Let us consider a solution curve $B(\tau) > 0$ such that $\lim_{\tau \rightarrow 0} B(\tau) = 0$. By hypothesis, $X^1(\tau), \dots, X^{n+1}(\tau)$ are finite for $\tau \rightarrow 0$. Then, by continuity, such a solution can be extended to $\tau = 0$, i.e., $T = 0$ cannot be a leaf. This happens as a consequence of well-known theorems on the ordinary differential equations, (see [52], pp 67–8). It holds

Result 3. *Let us assume that $\omega \in C^1(\mathcal{D} \cup \partial\mathcal{D})$. Then, for any functions $X^1(\tau), \dots, X^{n+1}(\tau) \in C^1([0, 1])$ the Cauchy problem*

$$\begin{aligned} \frac{dB}{d\tau} &= \sum_i \tilde{\xi}_i(B(\tau), X^1(\tau), \dots, X^{n+1}(\tau)) \frac{dX^i}{d\tau} \\ B(0) &= 0 \end{aligned}$$

allows only the solution $B = 0$, i.e., $T = 0$ is a leaf.

Proof. The proof is a trivial consequence of $\tilde{\xi}_i(0, X^1(0), \dots, X^{n+1}(0)) = 0$ for all $i = 1, \dots, n+1$ and of the standard existence and uniqueness theorem for solutions of ordinary differential equations [52]. \square

The same result holds true with obvious changes in the case where coordinates y^0, \dots, y^{n+1} introduced in section 5.5 are used. *A priori*, one can consider also a Pfaffian form ω such that it is continuous at the boundary $T = 0$ but non-necessarily C^1 there. The uniqueness of the solution of (47) with initial condition at the surface $T = 0$ could be ensured if the functions $\xi_i(U, X^1, \dots, X^{n+1})$ are locally Lipschitzian with respect to U uniformly with respect to X^1, \dots, X^{n+1} in a neighbourhood of $(U_0, X_0^1, \dots, X_0^{n+1})$. If even this condition fails, then the continuity of ω , i.e., the continuity of ξ also in $T = 0$, can allow multiple solutions of the differential equation (47). Note that, in the case there exist two solutions of the Cauchy problem for the Cauchy problem (50), 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 the case of existence of the limit as $B \rightarrow 0^+$ of the entropy, when (N) is violated, there are surfaces $S = \text{const}$ which are tangent to the submanifold $T = 0$ (see section 5.6.2).

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 $T = 0$. In the neighbourhood of any point belonging to $T = 0 \Leftrightarrow B = 0$, 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 an $S = \text{const}$ integral manifold, because of the integrability condition. 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 S - T diagrams one finds in standard textbooks on thermodynamics (cf also the definition of $P(x)$ transformations in [1]).

We now prove the main result of this section:

Result 4. *Let us consider \mathcal{D} described by means of the coordinates (B, X^1, \dots, X^{n+1}) introduced in subsection 5.5;*

let $\delta Q_{\text{rev}} \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \partial\mathcal{D})$ be integrable;

let S be continuous at $T = 0$, i.e., at $B = 0$.

Then (N) holds if and only if $B = 0$ is a leaf of the thermodynamic manifold $\mathcal{D} \cup \partial\mathcal{D}$.

Proof. The implication $(N) \Rightarrow \{B = 0 \text{ is a leaf}\}$ follows trivially from the fact that $S(B, X^1, \dots, X^{n+1}) > 0$ for any $B > 0$ and any X^1, \dots, X^{n+1} . Thus, there is no isentropic path starting in \mathcal{D} and reaching $B = 0$, i.e., $B = 0$ is a leaf of the thermodynamic foliation. (Note also that the same would be true in the case one finds $\lim_{B \rightarrow 0^+} S(B, X^1, \dots, X^{n+1}) \equiv \Sigma_0$ with Σ_0 a positive constant (this note is useful for [51]).)

The implication $\{B = 0 \text{ is a leaf}\} \Rightarrow (N)$ can be proved by showing that a violation of (N) implies that $B = 0$ cannot be a leaf. In fact, if (N) is violated and $\lim_{B \rightarrow 0^+} S(B, X_0^1, \dots, X_0^{n+1}) \equiv S(0, X_0^1, \dots, X_0^{n+1})$, then the inner integral manifold $0 < S(0, X_0^1, \dots, X_0^{n+1}) = \text{const}$ 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

$$X \equiv X^1, \dots, X^{n+1}. \quad (50)$$

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 neighbourhood of $(0, X_0)$. Such a point surely exists if (N) is violated, as it is easy to show (cf also [51]). We are interested in the zeros of the function

$$\sigma(B, X) \equiv S(B, X) - S(0, X_0). \quad (51)$$

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 is evident from (42).

In particular, we wish to know if there is a continuous function $B(X)$ defined in a neighbourhood 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 neighbourhood of $(0, X_0)$ where $\sigma(B, X) > 0$, thus the aforementioned function $B(X)$ does not exist. If it is a weak local minimum, in the sense that $S(0, X_0) \leq S(B, X)$ in a neighbourhood 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 neighbourhood $W \supset [0, B_0) \times V$ 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, $(0, X_0)$ being a local minimum, one can find a smaller neighbourhood where $S(B, X) = S(0, X_0)$ is impossible for any $B > 0$ ($S(0, X) = S(0, X_0)$ is instead allowed).⁵

In any convex neighbourhood 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 neighbourhood 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 $Z(\sigma) \equiv \{(B^0, X^0) \mid \sigma(B^0, X^0) = 0\}$, which is a closed set because σ 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

$$\bar{\sigma}(B, X) \equiv \begin{cases} \sigma(B, X) & \text{for } B \geq 0 \\ S(0, X) - S(0, X_0) + B & \text{for } B < 0. \end{cases} \quad (52)$$

This function $\bar{\sigma}(B, X)$ is a continuous function which is monotone strictly increasing in B also for $B < 0$. We have then extended σ to negative values of B , which is shown to be a 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 $\bar{\sigma}(0, X_0) = 0$. By the monotonicity property one has that there exist $B_1 < 0 < B_2$ such that $\bar{\sigma}(B_1, X_0) < 0 < \bar{\sigma}(B_2, X_0)$. By continuity, there exists an open neighbourhood $R \ni X_0$ such that $\bar{\sigma}(B_1, X) < 0 < \bar{\sigma}(B_2, X)$ for all $X \in R$. Then, from the intermediate value theorem it follows that there exists a value $\bar{B} \in (B_1, B_2)$ such that $\bar{\sigma}(\bar{B}, X) = 0$ for any fixed $X \in R$. Monotonicity ensures that \bar{B} is unique for each fixed $X \in R$. The function $B(X) : R \rightarrow \mathbb{R}$ is then defined as the map defined by $B(X) = \bar{B}$, where \bar{B} is the solution of $\bar{\sigma}(\bar{B}, X) = 0$ 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 $\bar{\sigma}$ is a continuous function which is monotonically strictly increasing in B . Being continuous, one has that the set

$$Z(\bar{\sigma}) \equiv \{(B, X) \mid \bar{\sigma}(B, X) = 0\} \quad (53)$$

⁵ Note 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 δQ_{rev} (this means that isentropic states are path-connected (cf [43])). In fact, in homogeneous thermodynamics, there exists an integral manifold of δQ_{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. Note 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 .

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

It is evident that

$$Z(\bar{\sigma}) \supseteq Z(\sigma) \quad (54)$$

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 neighbourhood of $(0, X_0)$ there exist points $(0, X^-)$ such that $S(0, X^-) - S(0, X_0) < 0$. Thus, being a spurious solution not defined in the whole R , the above proof allows us to conclude that $B(X) \geq 0$ surely exists. \square

The same result holds true in the case where coordinates y^0, \dots, y^{n+1} introduced in section 5.5 are used. One has to note that $\partial S / \partial y^0 = a_0 / T$ is a monotone function near $y^0 = 0$ because a_0 is of definite sign in a right neighbourhood of $y^0 = 0$ (one can impose $a_0(y^0 = 0, y^1, \dots, y^{n+1}) > 0$). This monotonicity is sufficient in order to implement the above proof, with straightforward changes. We now discuss some consequences of the above result.

5.6.1. 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. The validity of (N) does not forbid the inner leaves to asymptotically approach $T = 0$ as some deformation variable, say X^k , is allowed to diverge: $|X^k| \rightarrow \infty$ as $B \rightarrow 0^+$. The unattainability is clearly ensured because of such a divergence. Let us consider $X^1 = X_0^1, \dots, X^n = X_0^n = \text{const}$ and let us define $Y \equiv X^{n+1}$; then, it is evident that the differential equation

$$\frac{dB}{dY} = \tilde{\xi}_{n+1}(B, Y; X_0^1, \dots, X_0^n) \quad (55)$$

cannot allow a solution such that $B(Y) \rightarrow 0$ for $Y \rightarrow Y_0$ (with Y_0 finite) or such a solution could be extended at $B = 0$, against (N). Some examples are given below.

5.6.2. Violation of (N). From result 4, it follows that, when (N) is violated, there exists a solution $B(X)$ of $\delta Q_{\text{rev}} = 0$ such that $\lim_{X \rightarrow X_0} B(X) = 0$; 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 ω . As a consequence, for inner points $B(X)$ is at least C^2 . One can also calculate the gradient of $B(X^1, \dots, X^{n+1})$:

$$\left(\frac{\partial B}{\partial X^1}, \dots, \frac{\partial B}{\partial X^{n+1}} \right) = (\tilde{\xi}_1, \dots, \tilde{\xi}_{n+1}) \quad (56)$$

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

$$\left(\frac{\partial B}{\partial X^1}, \dots, \frac{\partial B}{\partial X^{n+1}} \right) \rightarrow 0 \quad \text{for } B \rightarrow 0^+ \quad (57)$$

i.e., $B(X)$ reaching $B = 0$ is tangent to $B = 0$.

5.6.3. Examples. Let us consider

$$\omega = dU + \frac{2}{3} \frac{U}{V} dV; \quad (58)$$

the domain is chosen to be $0 \leq U, 0 < V$ and the Pfaffian form ω is C^1 everywhere. One has $f = \frac{2}{3}U$ which vanishes for $U = 0$. The boundary $U = 0$ is an integral submanifold of ω .

Let us consider the Cauchy problem

$$\frac{dU}{dV} = -\frac{2}{3} \frac{U}{V} \quad (59)$$

$$U(V_0) = 0. \quad (60)$$

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 $S = c_0 U^{3/5} V^{2/5}$ and $T = 5/(3c_0)(U/V)^{2/5}$ (c_0 is an undetermined constant). (N) is satisfied. Along an isentropic surface $S_0 > 0$, one finds

$$U = \left(\frac{S_0}{c_0}\right)^{5/3} V^{-2/3} \quad (61)$$

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

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

$$\omega = dU + \left(\frac{U}{V}\right)^{2/3} dV \quad (62)$$

the Pfaffian form ω is not C^1 at the boundary $U = 0$. One has $f = U + U^{2/3} V^{1/3}$ which vanishes for $U = 0$. The Cauchy problem

$$\frac{dU}{dV} = -\left(\frac{U}{V}\right)^{2/3} \quad (63)$$

$$U(V_0) = 0 \quad (64)$$

allows two solutions: $U = 0$ and $U = (V_0^{1/3} - V^{1/3})^3$. The latter solution holds for $0 < V \leq V_0$, and it can be easily identified with the isentrope $S = S_0 = c_0 V_0$, 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 by the low-temperature behaviour of a Fermi gas. The Pfaffian form one takes into account is

$$\omega = dU + \frac{2}{3} \frac{U}{V} dV - \left(-\frac{1}{3} \frac{U}{N} + 2c(NV)^{2/3}\right) dN \quad (65)$$

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

$$f = 2U - 2c \frac{N^{5/3}}{V^{2/3}}. \quad (66)$$

Then the zero of the integrating factor occurs for

$$U = c \frac{N^{5/3}}{V^{2/3}} \quad (67)$$

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

$$B = U - c \frac{N^{5/3}}{V^{2/3}}. \quad (68)$$

This coordinate transformation is regular in $B = 0$. We have

$$\bar{p}(B, V, N) = \frac{2}{3} \frac{B}{V} \quad (69)$$

$$\bar{\mu}(B, V, N) = -\frac{1}{3} \frac{B}{N} \quad (70)$$

and

$$\bar{f} = 2B. \quad (71)$$

Then, one finds

$$S = \alpha B^{1/2} V^{1/3} N^{1/6} \quad (72)$$

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

$$S = \alpha (UV^{2/3}N^{1/3} - cN^2)^{1/2}. \quad (73)$$

Note that, along $S = S_0 = \text{const}$ one has

$$B = \left(\frac{S_0}{\alpha}\right)^2 \frac{1}{V^{2/3}N^{1/3}} \quad (74)$$

which can approach $B = 0$ only for $V \rightarrow \infty$ and/or $N \rightarrow \infty$. Moreover,

$$T = \frac{2}{\alpha} (UV^{2/3}N^{1/3} - cN^2)^{1/2} N^{-1/3} V^{-2/3} \quad (75)$$

and $\partial T / \partial U$ diverges as $T \rightarrow 0^+$.

5.7. Conditions for the validity of (N)

Let us define $X \equiv X^1, \dots, X^{n+1}$; B, X^1, \dots, X^{n+1} are regular coordinates adapted to the boundary as in section 5.5. We can write

$$\hat{S}(B, X) - \hat{S}(B_0, X) = \int_{B_0}^B dY \frac{1}{f(Y, X)}. \quad (76)$$

When $B_0 = 0$ or $B \rightarrow 0^+$ the integral has to be intended as an improper integral. Nevertheless, according to a common use, we bypass this specification in the following. We can show that it holds

Result 5. *If B, X^1, \dots, X^{n+1} are regular coordinates adapted to the boundary as in section 5.5 and if $\omega \in C^1(\mathcal{D} \cup \partial\mathcal{D})$, then $\hat{S} \rightarrow -\infty$ for $B \rightarrow 0^+$, which means that $S \rightarrow 0^+$ as $B \rightarrow 0^+$, i.e. (N) holds.*

Proof. One has

$$\begin{aligned} \xi_i(B, X^1, \dots, X^{n+1}) &= \xi_k(B, X^1, \dots, X^{n+1}) - \xi_k(0, X^1, \dots, X^{n+1}) \\ &= \frac{\partial \xi_k}{\partial B}(0, X^1, \dots, X^{n+1})B + o(B) \end{aligned} \quad (77)$$

(where $o(B)/B \rightarrow 0$ as $B \rightarrow 0$) and

$$f = k(0, X^1, \dots, X^{n+1})B + o(B) \quad (78)$$

where $k(0, X^1, \dots, X^{n+1})$ is continuous and positive because $f \geq 0$. As a consequence, near $B = 0$ the integrand behaves as follows:

$$\frac{\omega}{f} \sim \frac{1}{kB} dB. \quad (79)$$

Then the integral diverges as $\log(B)$ for $B \rightarrow 0^+$. There exists a function $\phi(B)$ non-integrable near $B = 0$ such that $1/f(B, X) > \phi(B)$:

$$\phi(B) = \inf_{(X^1, \dots, X^{n+1}) \in C} \left(\frac{1}{k(0, X^1, \dots, X^{n+1})} \right) \frac{1}{B} \quad (80)$$

where C is any open bounded set contained in \mathcal{D} (cf appendix B). \square

As a consequence of this result, we can conclude that any violation of (N) is involved with a Pfaffian form that is not C^1 also at the boundary $T = 0$, as can be easily verified by considering the examples violating (N) in section 6. Note that the same result holds true with obvious changes in the case where coordinates y^0, \dots, y^{n+1} introduced in section 5.5 are used. Naively, result 5 could be expected also on the grounds of the fact that, if ω is C^1 everywhere, then also f is C^1 everywhere. If one considers $\partial f/\partial U = 1 + S(\partial T/\partial U)$ and takes into account that the heat capacity at constant deformation parameters $(\partial U/\partial T) \rightarrow 0^+$ as $T \rightarrow 0^+$ if S is finite in the same limit, then $S \rightarrow 0$ in order that $\partial f/\partial U$ is continuous at $T = 0$. Positivity and concavity of S force S to be finite, as shown in section 6.

5.8. Condition (HOM)

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

$$\frac{\delta Q_{\text{rev}}}{f} = \frac{dS}{S}. \quad (81)$$

Let us consider $\int_{\gamma^0} \delta Q_{\text{rev}}/f$, where γ^0 is a curve having final point at temperature $T = 0$. If (N) holds, then $\int_{\gamma^0} \delta Q_{\text{rev}}/f$ is an improper integral which diverges to $-\infty$. In fact, if (N) holds, whichever the path γ^0 one chooses, the integral of dS/S diverges to $-\infty$ as $T \rightarrow 0^+$. If, instead, $\int_{\gamma^0} \delta Q_{\text{rev}}/f \rightarrow -\infty$, whichever path is chosen for reaching $T = 0$, then $S \rightarrow 0^+$ in the same limit. Then the following result holds:

Result 6. $(N) \Leftrightarrow \int_{\gamma^0} \delta Q_{\text{rev}}/f \rightarrow -\infty$ as $T \rightarrow 0^+$ whichever path is chosen (condition (HOM) in the following).

Note that, because of the concavity of S , one cannot have $\int_{\gamma} \delta Q_{\text{rev}}/f \rightarrow +\infty$ as $T \rightarrow 0^+$, because a non-negative and concave entropy cannot diverge (cf section 6). Thus, once the concavity property for S is ensured (cf [43]), one has only to check if the above integral diverges along any rectifiable curve approaching the surface $T = 0$.

Note that, in this form, the above theorem allows us 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 $T \rightarrow 0^+$.

If (N) is violated and the limit $\lim_{T \rightarrow 0^+} S$ exists, then (81) 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

$$\omega = dU + \left(\frac{U}{V} + \alpha_0 \frac{U^{2/3}}{(VN)^{1/3}} \right) dV + \left(\frac{U}{N} + \beta_0 \frac{U^{2/3}}{(VN)^{1/3}} \right) dN \quad (82)$$

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

$$f = 3U + \alpha_0 \frac{(UV)^{2/3}}{N^{1/3}} + \beta_0 \frac{(UN)^{2/3}}{V^{1/3}}. \quad (83)$$

The integrating factor f vanishes as $U \rightarrow 0$. ω/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 $U \rightarrow 0^+$. If $V/N = -\beta_0/\alpha_0$, then $f \sim 3U$ as $U \rightarrow 0^+$ and ω/f is no longer integrable near $U = 0$. Note that the entropy which corresponds to this Pfaffian form is $S = 3(UVN)^{1/3} + \alpha_0 V + \beta_0 N \geq 0$. (N) is violated and S vanishes in the submanifold $U = 0, V/N = -\beta_0/\alpha_0$.

Note that, if S is not concave but simply positive, then condition (HOM) is still equivalent to (N), and that (HOM) is not affected by the connectedness properties of $f = 0$.

5.9. Inaccessibility (C) and the failure of (N)

The violation of (N) is 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 an 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’ [53]. It is also evident that the Carnot–Nernst cycle discussed in appendix 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 an isentropic path at $T > 0$ reaching the absolute zero of the temperature). Moreover, the approach to the problem by means of δQ_{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 [54] 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

$$\Sigma_0 < \inf_{X^1, \dots, X^{n+1}} \Sigma(X^1, \dots, X^{n+1}). \quad (84)$$

One could then impose that $\Sigma_0 = 0$ for all the systems, which would allow us to recover a universal behaviour. Even the adiabatic inaccessibility would be restored, because the second law would inhibit reaching $T = 0$ adiabatically. This behaviour 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.

6. Notes on the Gibbsian approach

We recall that in the Gibbsian approach [55], the existence of the entropy is a postulate, because the entropy appears in an axiomatic framework (see also [47, 56, 20]). In a certain sense, very loosely speaking, Gibbs starts where Carathéodory leaves off [57]. This can be considered the reason why in the 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:

$$S = S(U, X^1, \dots, X^{n+1}) \quad (85)$$

where, as usual, X^1, \dots, 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 [58, 59]).

6.1. Extension of S to $T = 0$

Let us define

$$I(U, X^1, \dots, X^{n+1}) = -S(U, X^1, \dots, X^{n+1}). \quad (86)$$

In what follows, x stays for a state in the thermodynamic manifold: $x \equiv (U, X^1, \dots, X^{n+1})$. The function $I(x)$ is, by definition, a convex function and a positively homogeneous function. As a consequence, its epigraph is a convex cone. This convex function I is defined on \mathcal{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 $I(x)$ at the boundary $\partial\mathcal{C}$ and obtain again a convex function. This is done as follows [59]: I can be extended to the set

$$\mathcal{F} = \mathcal{C} \cup \partial\mathcal{C}_f$$

where

$$\partial\mathcal{C}_f \equiv \{y \in \partial\mathcal{C} \mid \liminf_{x \rightarrow y} I(x) < \infty\}$$

and

$$I(y) \equiv \liminf_{x \rightarrow y} I(x) \quad \forall y \in \partial\mathcal{C}_f. \quad (87)$$

The above extension is convex on a convex set. In general, one cannot substitute $\liminf_{x \rightarrow y} I(x)$ with $\lim_{x \rightarrow y} I(x)$ because the latter may not exist [59]. Moreover, the behaviour of the convex function $I = -S$ at the boundary has to be such that

$$\liminf_{x \rightarrow x_0} I(x) > -\infty \quad (88)$$

for any x_0 belonging to the boundary of the convex domain (cf problem F, p 95 of [59]).

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 from 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 [1, 2]. In any case, the definition offered by the theory of convex functions

$$S(y) \equiv \limsup_{x \rightarrow y} S(x) \quad \forall y \in \partial\mathcal{C}_f \quad (89)$$

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 exist.

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

$$S(y) \equiv \lim_{x \rightarrow y} S(x) \quad \forall y \in \{T = 0\}. \quad (90)$$

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

$$\lim_{x \in \mathcal{D} \rightarrow x_b} G \quad (91)$$

exists.

It is still to be stressed that, for a non-negative concave S , one has to find $\lim_{T \rightarrow 0^+} S < \infty$ as a consequence of (88).

6.2. Attainment of the lower bound of S

The Gibbsian approach allows us to conclude immediately that, if the upper bound I_0 of I is attained, then it has to be attained at 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) [59]. Then, if the lower bound S_0 of S is attained, it is attained at the boundary of the domain of S . Moreover, under very simple hypotheses on the domain, the upper bound of I is actually attained [58, 59]. 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 note also that, the thermodynamic domain being a convex cone, there is no extreme point apart from the origin 0 of the cone (which cannot be considered a physically meaningful state [43]).

Note that, given the surface $T(U, X^1, \dots, X^{n+1}) = 0 \Leftrightarrow U = U_0(X^1, \dots, X^{n+1})$, then, for each point on this surface, as a consequence of the homogeneity of the entropy, it holds

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

At the same time, the homogeneity of degree zero of T implies

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

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

$$K_0 \equiv \{X_0^a \mid \lambda X_0^a \in K_0, \lambda > 0\} \quad (92)$$

is contained in the surface $T = 0$ because of the intensivity of T . As a consequence, in the 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.

6.3. 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 Landsberg's discussion about a multi-branching near $T = 0$ [2, 1], 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 vice versa (there is no possibility of finding two branches such as the ones in figure 1(a), because both have to start at $S = 0, T = 0$). A multi-branching can, e.g., be obtained by violating the concavity at least near $T = 0$. For an interesting example, see [54]. (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 $T = 0$.)

6.4. Violation of (N) and Landsberg's hypothesis

In Landsberg's analysis, the hypothesis is made that the unattainability of $T = 0$ can hold despite the violation of (N) if an abrupt discontinuity occurs near $T = 0$. Landsberg makes

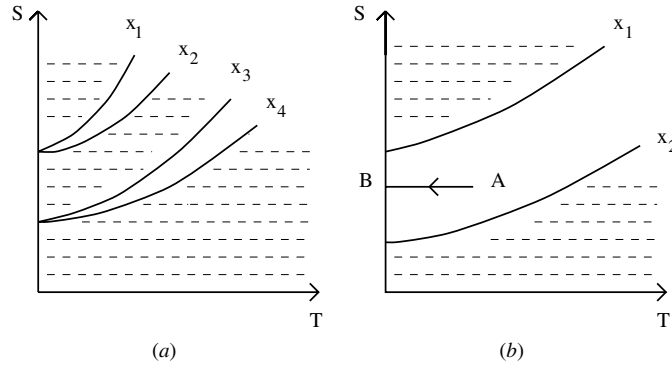


Figure 1. (a) Multi-branch structure of the thermodynamic space. According to Landsberg, it implies the validity of (U) and the violation of (N). (b) Violation of (N) that implies a violation of (U), due to the presence of the isentropic AB. Landsberg conjectures that (U) holds if a discontinuity near $T = 0$ occurs. In (a) and (b) the dashed regions are forbidden.

the example of an abrupt divergence in the elastic constants of a solid as a conceivable ideal process preventing a solid violating (N) reaching a zero-temperature state by means of quasi-static adiabatic volume variations (the hypothesis of [1] is compatible with the vanishing near $T = 0$ of the (adiabatic) compressibilities that are related to 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). We discuss this hypothesis briefly. Consider the following toy model:

$$S = \gamma_0 V^{1-\alpha} U^\alpha + \delta_0 V \tag{93}$$

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

$$T = \frac{1}{\gamma_0 \alpha} \left(\frac{U}{V} \right)^{1-\alpha} \tag{94}$$

which vanishes as $U \rightarrow 0^+$: $T = 0 \Leftrightarrow U = 0$. 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. (Note that in this example the domain is not a convex cone because we introduce a lower bound V_0 for V , as is physically reasonable in order to justify thermodynamics on statistical mechanical grounds. 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 $\delta_0 > 0$, then (N) is violated and S can assume an interval of values at $T = 0$. If $\delta_0 = 0$, then (N) is satisfied and I is maximal for $U = 0$. A special case is represented by the photon gas, where $\alpha = \frac{3}{4}$.

This toy model corresponds to the following behaviour of S as a function of T and V :

$$S(T, V) = (\epsilon_0 T^{\frac{\alpha}{1-\alpha}} + \delta_0) V \tag{95}$$

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

$$U = \left(\frac{S - \delta_0 V}{\gamma_0} \right)^{\frac{1}{\alpha}} V^{\frac{\alpha-1}{\alpha}}. \tag{96}$$

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

$$T = \frac{1}{\alpha} \frac{1}{\gamma_0^{\frac{1}{\alpha}}} V^{\frac{\alpha-1}{\alpha}} (S - \delta_0 V)^{\frac{1}{\alpha}-1} \tag{97}$$

the pressure is

$$p = \frac{1}{\alpha} \left(\frac{1}{\gamma_0} \right)^{\frac{1}{\alpha}} (S - \delta_0 V)^{\frac{1}{\alpha}-1} V^{-\frac{1}{\alpha}} (S(1 - \alpha) + V\alpha\delta_0). \quad (98)$$

The isentropic $S = S_0$ has the equation

$$U(V) = \left(\frac{S_0 - \delta_0 V}{\gamma_0} \right)^{\frac{1}{\alpha}} V^{\frac{\alpha-1}{\alpha}} \quad (99)$$

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:

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S. \quad (100)$$

In our case, we get

$$K_S = \alpha^2 \gamma_0^{\frac{1}{\alpha}} \frac{1}{1 - \alpha} \frac{1}{S^2} V^{\frac{1}{\alpha}} (S - \delta_0 V)^{\frac{2\alpha-1}{\alpha}} \quad (101)$$

and three cases occur: when $\frac{1}{2} < \alpha < 1$ then $K_S \rightarrow 0$ as $T \rightarrow 0^+$, in such a way that the elastic constants of the system diverge in that limit, forbidding any further expansion (Landsberg's behaviour); when $0 < \alpha < \frac{1}{2}$ then $K_S \rightarrow \infty$ as $T \rightarrow 0^+$, the elastic constants vanish and the behaviour of the system is pathologic (the system appears to be 'totally deformable' in that limit); when $\alpha = \frac{1}{2}$ then $K_S \rightarrow \gamma_0^2 V^2 / (2S^2)$ which is in any case finite (S is surely positive and not zero) and a physical hindrance against reaching $T = 0$ is not apparent. For $\alpha = \frac{3}{4}$ the behaviour for S as $T \rightarrow 0^+$ is like the one of Debye model, except for the shift $\delta_0 V$ which allows the violation of (N); the adiabatic expansion stops at $T = 0$ because of a vanishing K_S . For $\alpha = \frac{1}{2}$ one obtains a behaviour similar to that of an electron gas near $T = 0$, except for the shift $\delta_0 V$; no vanishing or divergence of K_S is allowed at $T = 0$.

We wish to underline that, if one considers the entropic fundamental equation of an electron gas at low temperature and shifts it by $\delta_0 V$, then the situation is still different, because of the zero-point mode contribution. In fact, such a contribution allows us to get a positive and finite p as $T \rightarrow 0^+$ and, moreover, a positive and finite $K_{S,N}$ as $T \rightarrow 0^+$ (the domain is $V > 0, N > 0, U \geq U_0(V, N)$, where N is the particle number). As a consequence, Landsberg's mechanism does not seem to be available. Instead, even if the zero-point mode contribution is taken into account in the case of a Debye crystal, the pressure is still positive as $T \rightarrow 0^+$ but $K_{S,N}$ vanishes. A further property is described in appendix C.

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 belonging to 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 behaviour (i.e., a behaviour which does not appear in other models).

7. Conclusions

We have discussed the status of the third law of thermodynamics and we have given an heuristic argument in favour of the entropic version of the third law. Then, we have analysed 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 δQ_{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 hypersurface of the Pfaffian form δQ_{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 of obtaining 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 [51], 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 [46]. Also in the quasi-homogeneous case (N) holds iff $\lim_{T \rightarrow 0^+} S = 0$. The analysis of sections 5.5 and 5.6 holds with obvious changes; moreover, condition (HOM) holds unaltered, and, if the Pfaffian form ω is C^1 everywhere, then (N) holds (this can be shown by using a criterion analogous to the one appearing in result 5).

Acknowledgments

The author wishes to thank Lawrence Conlon for his clarifying e-mail on the Frobenius theorem in the presence of manifolds with boundary.

Appendix A. Transformations at $T = 0$

Concerning the hypothesis (η_1) of section 3, 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 special Carnot cycle having the lower isotherm at $T = 0$ (see figure 2). We refer to this cycle as 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 formulation of the second law which is implicit in 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 absolute zero (see also [60]).

Criticisms against this path, relating the third law to the second one, have a long history (see [2, 14, 18, 53, 61, 62] and references therein) which starts with Einstein's objection. Einstein

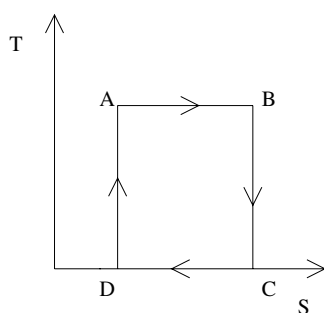


Figure 2. Carnot–Nernst cycle in the plane T – S .

underlines that near $T = 0$ dissipations begin being non-negligible [53]. 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., [14]). The objection against the Carnot–Nernst cycle can also avoid referring to irreversibility arising near $T = 0$, as discussed, e.g., in [61, 62]. 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 figure 2). Then, it does not seem possible for the system to be carried along the CD transformation contained in the $T = 0$ surface [61, 62] 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 any reversible transformation at $T = 0$ is adiabatic by itself, thus, from the point of view of an operative procedure, one should implement an adiabatic insulation of the system.

This kind of reasoning implies a failure of the thermodynamic formalism at $T = 0$, because of the impossibility of giving a satisfactory prescription for implementing transformations at $T = 0$. In particular, the problem is related to 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 us 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 [53, 61, 62]. Nevertheless, we wish to underline that, as a matter 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, *it corresponds to a path mathematically distinguished in the thermodynamic space*. It is clear that, if one considers a system described by (U, V, N) and, in ideally approaching $T = 0$ considers the system as closed, then no possibility of distinguishing operatively between the adiabatic transformation implemented in order to approach $T = 0$ and the adiabatic transformation $T = 0$ is left. But for systems with a larger thermodynamic space (e.g., systems characterized by other deformation parameters) one could have closed systems where the adiabatic and isothermal transformation at $T = 0$ could be implemented.

Appendix B. A sufficient condition for a continuous S at $T = 0$

The entropy S is required to be continuous at $T = 0$. This can be obtained as follows. It is evident that the continuity of \hat{S} implies the continuity of S . Then, one can impose conditions

which allow \hat{S} to be continuous at $T = 0$. Nevertheless, the continuity of \hat{S} excludes, by direct inspection, the possibility of obtaining $S = 0$ at $T = 0$. Thus, one has to find further conditions on \hat{S} in order to allow the possibility of getting a vanishing entropy at $T = 0$. Let us consider

$$\hat{S}(B, X^1, \dots, X^{n+1}) = \int_{B_0}^B dB \frac{1}{f(B, X^1, \dots, X^{n+1})} + \hat{S}(B_0, X^1, \dots, X^{n+1}). \quad (\text{B.1})$$

We wish to know if the limit as $B \rightarrow 0^+$ of \hat{S} exists. A sufficient condition is the following: there exists a positive function $\phi(B)$ such that for all $B \in (0, B_0]$ and for all $X^1, \dots, X^{n+1} \in C$

$$\frac{1}{f(B, X^1, \dots, X^{n+1})} < \phi(B) \quad (\text{B.2})$$

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

$$\lim_{B \rightarrow 0^+} \int_{B_0}^B dB \phi(B) < \infty. \quad (\text{B.3})$$

Then $\int_{B_0}^B dB 1/f$ is uniformly convergent and, \hat{S} being continuous for $B > 0$, one finds that \hat{S} can be extended continuously also at $B = 0$. This condition ensures that (N) is violated. The above condition does not leave room for $S = 0$ for some (but not all) values of $X^1, \dots, X^{n+1} \in \mathcal{D}$. Actually, continuity on a open bounded subset $R \subset \mathbb{R}^{n+1} \cap \mathcal{D}$ of the allowed values for the variables X^1, \dots, X^{n+1} , can also be obtained by assuming that (B.2) holds on R and not for any open bounded set C contained in \mathcal{D} . In this case, \hat{S} is continuous at $T = 0$ for $X^1, \dots, X^{n+1} \in R$.

In order to obtain a condition ensuring (N) a sufficient condition is the following: there exists a positive function $\phi(B)$ such that for all $B \in (0, B_0]$ and for all $X^1, \dots, X^{n+1} \in C$

$$\frac{1}{f(B, X^1, \dots, X^{n+1})} > \phi(B) \quad (\text{B.4})$$

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

$$\lim_{B \rightarrow 0^+} \int_{B_0}^B dB \phi(B) = -\infty. \quad (\text{B.5})$$

Then, because the above divergence of the integral is uniform in X^1, \dots, X^{n+1} , one finds that $\hat{S} = \log(S) \rightarrow -\infty$ as $T \rightarrow 0^+$, i.e. $S \rightarrow 0^+$ as $T \rightarrow 0^+$. The same considerations hold true if coordinates y^0, \dots, y^{n+1} are used.

Appendix C. A further property in the Gibbsian frame

Another point that can be underlined is the following. Let us assume the extension of 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 [63] for the internal energy U . Then I is a closed proper convex function which is *essentially smooth*, that is, $|\nabla I| \rightarrow \infty$ for any subsequence converging to a boundary point. In fact, in the gradient of I the factor $1/T$ appears which diverges as the boundary $T = 0$ is approached. This allows us 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. (cf, e.g., [63]). But we think that the entropy representation is more fundamental with respect to the energy representation at least as far as the boundary $T = 0$ is to be taken into account.

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