Notes on the third law of thermodynamics: II

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Abstract
We develop further our analysis of the third law of thermodynamics; in particular, we discuss further conditions ensuring the validity of the third law of thermodynamics in its entropic form (N). The introduction in standard homogeneous thermodynamics of the framework in which the absolute temperature T appears as an independent coordinate for the entropy S is followed by the introduction of a more general framework in which Gibbs thermodynamic space, where only extensive independent coordinates appear, is suitably generalized. General properties of S are also discussed. An analysis of the differential conditions which can ensure the validity of (N) follows. Then, we introduce a condition involving the behaviour of generalized heat capacities along curves leaving the surface $T = 0$ and we show that, under suitable mathematical conditions, it is equivalent to (N). The physical meaning of this condition is also clarified, and amounts to the impossibility for a system to leave a state at $T = 0$ without heat absorption. Then, we show that a condition of minimum entropy at $T = 0$ is again equivalent to (N) under suitable conditions. Some notes about (N) when one allows deformation coordinates to be divergent as $T \to 0^+$ and about phase coexistence and mixtures also appear.

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1. Introduction

In this paper, we discuss some further aspects of the third law of thermodynamics in its entropic form. In [1] a discussion of the third law, both in Carathéodory's approach and Gibbs' one, has been presented in the framework of standard homogeneous thermodynamics. Herein, we allow a more general framework and we also use T as an independent thermodynamic variable. Then, we discuss the differential conditions ensuring (N) and we present a condition involving the behaviour of generalized heat capacities as $T \to 0^+$ and show that it is equivalent to (N). A related condition in the Gibbsian frame, a condition of minimum entropy and its relation with (N) are discussed, and a summary of conditions leading to (N) is presented. Some notes

about the validity of (N) when deformation coordinates are allowed to diverge and about phase coexistence and mixtures also appear. For an introduction to the third law of thermodynamics and for an extensive list of papers concerning the third law, we refer the reader to [1].

As far as the unattainability version (U) of the third law and its relation to (N) are concerned, we limit ourselves to a short discussion about the de-linking of (U) with respect to (N) in section 8 and in appendix B, referring the reader to Landsberg's works [2, 3] and also to [4] for an extensive discussion concerning the relation between (U) and (N); see also [5].

The plan of the paper is as follows. In section 2, we discuss some properties of the thermodynamic domain also by using T as an explicit variable; an heuristic picture for non-homogeneous thermodynamics is also allowed; in section 3, we discuss some assumptions on S; section 4 differential criteria ensuring (N) are analysed. In section 5, a new condition for implementing (N) is introduced, and its physical meaning is discussed. A related condition is found in section 6. In section 7 the condition of minimum entropy at $T = 0$ and its relation to (N) are discussed. In section 8 we present a short discussion of the violation of (N) which can occur as infinities in the deformation parameters are allowed. Section 9 contains notes about the relation between the heat theorem, phase coexistence and mixtures.

2. Nernst's heat theorem revisited: the framework

In the following, we consider first standard homogeneous thermodynamics and discuss the properties of the domain both in Gibbs space and in the frame where T appears as an independent variable. We point out that the Pfaffian form δQ_{rev} is non-singular in the former frame but it seems to be singular at $T = 0$ in the latter frame, due to a singular behaviour of the map $U \mapsto T$ at $T = 0$. We also give some explicit examples of this trouble. A very simple structure for the thermodynamic space is also given.

Then, we introduce a formal framework for non-homogeneous thermodynamics and make reasonable assumptions about the properties of the domain, generalizing those of standard thermodynamics.

2.1. Standard homogeneous thermodynamics

We have to distinguish two possible frameworks. We call the 'Gibbsian framework' the framework in which extensive variables are used as independent variables and one starts from the infinitesimal heat exchanged reversibly δQ_{rev} in order to recover the fundamental equation in the entropy representation (cf [1]). We think that this approach is more fundamental, from a theoretical point of view, with respect to the one in which T appears as an independent variable. In fact, the former is a framework where the non-singular character of the Pfaffian form δQ_{rev} is easily justified, moreover the discussion of the problem of $T = 0$ is well posed. The troubles arising in the other framework are simply due to the failure of the coordinate transformation $U \mapsto T$ to be a diffeomorphism, as it is shown below.

2.1.1. Gibbsian framework. The domain $\mathcal{D}$ of S is assumed to be an open convex cone [1, 6]. Independent variables are $(U, V, X^1, \ldots, X^n)$. One could also assume that the domain of $S(U, V, X^1, \ldots, X^n)$ is a convex cone of the form

$$\mathcal{D} \cup \partial \mathcal{D} = \{(U, V, X^1, \ldots, X^n) \,|\, (V, X^1, \ldots, X^n) \in \mathcal{K}, U \geqslant b(V, X^1, \ldots, X^n)\} \tag{1}$$

where $\mathcal{K}$ is a convex cone and $b(V, X^1, \ldots, X^n)$ is an extensive convex function (bounded from below) which can be construed as the ground-state energy (cf [1, 6]). The range of U

is an interval bounded and closed from below. It is also useful to introduce a new variable $B = U - b$, which is such that $B \geqslant 0$ and $B = 0 \Leftrightarrow T = 0$.

2.1.2. Framework with T replacing U. This is a common framework in thermodynamics. It can be obtained by inverting the relation between T and U. In passing from $(U, V, X^1, \ldots, X^n)$ to $(T, V, X^1, \ldots, X^n)$, one obtains the following structure from (1), $\mathcal{D} \cup \partial \mathcal{D} = I_T \times \mathcal{K}$, where $I_T = \{T \geqslant 0\}$. $T = T(U, V, X^1, \ldots, X^n)$ can be inverted to give $U(T, V, X^1, \ldots, X^n)$ if $\partial T / \partial U \neq 0$. It is to be noted that

$$\frac{\partial T}{\partial U} = \frac{1}{C_{V, X^1, \ldots, X^n}} \tag{2}$$

where C is the heat capacity at constant $V, X^1, \ldots, X^n$. As far as $C_{V, X^1, \ldots, X^n} \to 0$ when $T \to 0^+$, which is a necessary condition for a finite entropy in the limit as $T \to 0^+$, the coordinate transformation $U \mapsto T$ is singular at $T = 0$. This is mostly evident if the inverse transformation $T \mapsto U$ is performed. This means that $U \mapsto T$ is not a diffeomorphism. One gets a representation of the Pfaffian form which holds everywhere except at the boundary $T = 0$, where a singularity of the Pfaffian form appears as far as a non-negative definite concave S has to be finite at $T = 0$ (see [1], section 6). In the following, the deformation coordinates are indicated with $x^1, \ldots, x^{n+1}$. (We recall that we include constitutive coordinates in the set of deformation coordinates, as in [1].) In this representation, one has

$$\delta Q_{\text{rev}} = C_{x^1, \ldots, x^{n+1}}(T) \, dT + \sum_i T \frac{\partial S}{\partial x^i} \, dx^i. \tag{3}$$

Under suitable conditions, to be discussed in the following sections, each term in the above expression vanishes as $T \to 0^+$, thus the Pfaffian form seems to be singular at each point of the surface $T = 0$ in these coordinates (note that the Pfaffian form (3) in the case of the ideal gas is not singular at $T = 0$ because $C_{V,N} = \text{const}$, thus the map $U \mapsto T$ is regular at $T = 0$; nevertheless, the ideal gas model is pathological, because the entropy becomes negative for small values of T and, moreover, it diverges $S \to -\infty$ as $T \to 0^+$ and the third law is violated).

2.1.3. Examples. We show that a non-singular Pfaffian form which is C^1 everywhere in Gibbsian coordinates appears as a singular Pfaffian form in coordinates where T substitutes U, and, moreover, it can fail to be C^1 at $T = 0$. Let us consider

$$\delta Q_{\text{rev}} = dU + 2\frac{U}{V} \, dV \tag{4}$$

with $\mathcal{D} = \{U \geqslant 0, V > 0\}$. One obtains a concave entropy $S = U^{1/3} V^{2/3}$ (where an undetermined multiplicative constant is put equal to 1 for simplicity) and $T = 3U^{2/3} V^{-2/3}$. Moreover, one finds

$$\frac{\partial T}{\partial U} = 2U^{-1/3} V^{-2/3} \tag{5}$$

and the correspondence $U \longleftrightarrow T$ cannot be a diffeomorphism everywhere but only for $U > 0$, i.e. $T > 0$. By inverting, one gets $U = 3^{-3/2} T^{3/2} V$ and $S = 3^{-1/2} T^{1/2} V$. In these coordinates, we have

$$\delta Q_{\text{rev}} = \tfrac{1}{2} 3^{-1/2} T^{1/2} V \, dT + 3^{-1/2} T^{3/2} \, dV. \tag{6}$$

It is evident that both the coefficients of the Pfaffian form vanish when $T = 0$, but this is due to the peculiar nature of the coordinate change $U \mapsto T$; the first coefficient is not C^1 at $T = 0$, where its derivative with respect to T diverges. Note also that $\partial S / \partial T$ diverges as $T \to 0^+$.

Let us consider also the well-known photon gas. One has

$$\delta Q_{\text{rev}} = dU + \frac{1}{3}\frac{U}{V}\,dV \qquad (7)$$

which is defined for $U \geqslant 0$ and $V > 0$; moreover, $S = c_0 U^{3/4} V^{1/4}$. $T(U, V) = 0$ is obtained for $U = 0$. By finding $U(T, V)$ one gets $S(T, V) = c_1 V T^3$, where c_1 is a constant, and

$$\delta Q_{\text{rev}} = c_1 3 T^3 V\,dT + c_1 T^4\,dV. \qquad (8)$$

It is evident that both the coefficients of δQ_{rev} vanish in these coordinates at $T = 0$, i.e., the Pfaffian form seems to be singular if T is used as an independent coordinate.

2.2. Non-homogeneous thermodynamics

More in general, we wish to allow non-homogeneous thermodynamics (i.e., thermodynamics without homogeneity symmetry), which surely occurs when gravitational interaction becomes non-negligible. We limit ourselves to heuristic considerations which involve reasonable assumptions on S and on the domain. An example of construction of a non-homogeneous thermodynamics, which fits the properties of at least some self-gravitating systems, is found in [7].

The domain $\mathcal{D}$ is assumed to be an open simply connected set which is dense in its closure, in particular, near the boundary $T = 0$. This allows a unique extension to $T = 0$ by continuity of any continuous function h such that $\lim_{T \to 0^+} h$ exists. The aforementioned density property near $T = 0$ can be obtained, e.g., if, at least near $T = 0$, $\mathcal{D}$ can be written as a Cartesian product of intervals (one for each variable) $\mathcal{D} = I_T \times I_1 \times \cdots \times I_{n+1} \subset \mathbb{R}^{n+2}$, where $I_T = (0, T_0)$. One can also introduce a generalization of the Gibbs framework, where the thermodynamic space is described by (would-be extensive)[1] independent variables $U, X^1, \ldots, X^{n+1}$ and where one assumes that $S \geqslant 0$ and that $\partial S/\partial U = 1/T > 0$. U plays the role of internal energy and $S(U, X^1, \ldots, X^{n+1})$ should correspond to the fundamental relation in the entropy representation. The integrable Pfaffian form

$$\delta Q_{\text{rev}} = dU - \sum \xi_i\,dX^i \qquad (9)$$

(assumed to be at least in $C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$) is then everywhere non-singular, and a foliation of the thermodynamic manifold into adiabatic surfaces of codimension 1 can be given. In the presence of a transversal symmetry, an integrating factor can be straightforwardly found [6, 7].

Note that relaxing homogeneity has important consequences in the thermodynamic construction, and superadditivity of the entropy should be privileged in order to obtain a meaningful picture. See in particular [8, 9] for a general discussion on this topic and see, e.g., [7] for the case of quasi-homogeneous thermodynamics.

The set $T = 0$ is assumed to be a codimension 1 integral manifold of δQ_{rev}. In passing to coordinates where T is an independent coordinate, the Pfaffian form again seems to be singular in $T = 0$ because of the lack of regularity of the coordinate transformation $U \mapsto T$. Another hypothesis which can be made is that $T = 0$ corresponds also to a sort of ground-state energy $U_0 = b(X^1, \ldots, X^{n+1})$, with b bounded from below, in the sense that for the internal energy $U \geqslant b(X^1, \ldots, X^{n+1})$ holds, and, moreover, $U = b$ iff $T = 0$. The structure for the domain one can propose is then a generalization of the one for standard thermodynamics,

$$\mathcal{D} \cup \{T = 0\} = \{(U, X^1, \ldots, X^{n+1}) \,|\, (X^1, \ldots, X^{n+1}) \in \mathcal{K}, U \geqslant b(X^1, \ldots, X^{n+1})\} \qquad (10)$$

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[1] They are expected to be additive, i.e., if one considers a system which is composed of two non-interacting subsystems, then $X = X_1 + X_2$. See [8] and cf [7].

where $\mathcal{K} \subset \mathbb{R}^{n+1}$ is an open set (and, e.g., $b \in C^1(\mathcal{K})$). In order to implement superadditivity, this domain has to be closed under addition. The latter property can be obtained if $\mathcal{K}$ is closed under addition of the X^i variables and if b is subadditive; cf [7] for the quasi-homogeneous case. Then, by defining $B = U - b \geqslant 0$, one obtains a regular map $U \mapsto B$ where $T = 0$ iff $B = 0$. One finds $\mathcal{D} \cup \{T = 0\} = I_B \times \mathcal{K}$, where $I_B = [0, \infty)$. Moreover, $\partial S/\partial B = \partial S/\partial U = 1/T$. By defining for all $i = 1, \ldots, n + 1$

$$\tilde{\xi}_i(B, X^1, \ldots, X^{n+1}) \equiv \xi_i(B, X^1, \ldots, X^{n+1}) - \frac{\partial b}{\partial X^i}(B, X^1, \ldots, X^{n+1}) \quad (11)$$

one finds

$$\delta Q_{\text{rev}} = \mathrm{d}B - \sum_i \tilde{\xi}_i(B, X^1, \ldots, X^{n+1}) \, \mathrm{d}X^i \quad (12)$$

and it holds $\tilde{\xi}_i(B = 0, X^1, \ldots, X^{n+1}) = 0$ for all $i = 1, \ldots, n + 1$, $T = 0$ being an integral hypersurface of δQ_{rev} in our assumptions.

If one uses T as an independent coordinate, one finds $\mathcal{D} \cup \{T = 0\} = I_T \times \mathcal{K}$.

Another possibility is to describe in general the boundary $T = 0$ as a boundary of a differentiable manifold, as in section 5.5.1 of [1]. See appendix A for some comments involving the main results of this paper.

2.3. The boundary $T = 0$

Here we assume that the $T = 0$ is included in the domain of S as a function of T and that the surface $T = 0$ is connected (and also path-connected; with 'connected' we shall mean path-connected in the case of the surface $T = 0$). The latter assumption is related to the possibility of a multi-branching in the sense of Landsberg [2, 3]. We discuss in the following the relevance of this assumption and what can happen by relaxing it. We recall that, if S is continuous also at $T = 0$, connectedness of the surface $T = 0$ is relevant only in the case of non-homogeneous thermodynamics.

3. Properties of S

We assume an entropy S belonging at least to $C^1(\mathcal{D})$ and we consider the following independent variables: $(T, x^1, \ldots, x^{n+1})$.

We assume also the following:

(F) : $\lim_{T \to 0^+} S$ exists and is finite at $T = 0$ for any finite value of $x^1, \ldots, x^{n+1}$.

The existence of the limit ensures that S can be uniquely extended by continuity at $T = 0$, by hypothesis the set $\mathcal{D}$ being dense in its closure. An analogous extension by continuity is allowed for partial derivatives of S, if they are finite in the limit as $T \to 0^+$. The latter property[2] simplifies some mathematical aspects.

Note that, in the case of standard homogeneous thermodynamics, $\mathcal{D}$ is a convex set, thus it is dense in its closure. The extended domain is $\mathcal{D} \cup \{T = 0\}$. Moreover, the finiteness of the entropy at $T = 0$ is a consequence of the positivity and of the concavity of S [1]. If the limit of S as $T \to 0^+$ does not exist, then (N) is of course violated, as shown in [1].

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[2] In homogeneous thermodynamics in Gibbsian framework, S cannot be C^1 also at $T = 0$, because $\partial S/\partial U = 1/T$ is surely divergent in the limit as $T \to 0^+$. The same is true in Gibbs-like framework for non-homogeneous thermodynamics where one defines $\partial S/\partial U = 1/T$.

It is also useful to define

$$dS_T \equiv a_0(T, x^1, \ldots, x^{n+1}) \, dT$$

$$dS_\perp \equiv \sum_{i=1}^{n+1} a_i(T, x^1, \ldots, x^{n+1}) \, dx^i \tag{13}$$

which allow us to write $dS = dS_T + dS_\perp$.

Another important property which has to be discussed is the stability property (a): $C_{x^1,\ldots,x^{n+1}}(T) > 0$ for all $T > 0$, where $C_{x^1,\ldots,x^{n+1}}(T)$ is continuous everywhere in the domain. This property amounts to the requirement that S is a strictly monotonically increasing function of T. This property is automatically ensured in homogeneous thermodynamics, being associated with the concavity of the entropy. If it is violated in such a way that non-uniformity of the sign of the heat capacities along transformation reaching absolute zero is allowed, then the unattainability (U) and (N) in general do not imply each other, thus they can become essentially inequivalent [10]. See appendix B.

The finiteness condition (F) implies that in a right neighbourhood of $T = 0$ it holds that

$$\lim_{T \to 0^+} C_{x^1,\ldots,x^{n+1}}(T) = 0. \tag{14}$$

Equation (14) is a necessary but not sufficient condition for the integrability near $T = 0$ of $C_{x^1,\ldots,x^{n+1}}(T)/T$ [11] (e.g. $C_{x^1,\ldots,x^{n+1}}(T) \sim 1/(\log(1/T)) \to 0^+$ as $T \to 0^+$ gives rise to a non-integrable function $C_{x^1,\ldots,x^{n+1}}(T)/T$). A sufficient condition for the integrability is obtained if $C_{x^1,\ldots,x^{n+1}}(T) \sim T^\delta$ as $T \to 0^+$, where $\delta > 0$ (see also [11]). Note also that (14) is not a sufficient condition for (N) [12].

3.1. Heat capacity along a curve

It is useful to recall Clausius' definition of the entropy variation between two equilibrium states A, B, which consists in the calculation of the following line integral along a generic simple oriented curve γ (i.e. reversible transformation) joining A to B:

$$S(B) - S(A) = \int_{\gamma A \to B} \frac{\delta Q_{rev}}{T}; \tag{15}$$

in general, both deformation coordinates and the temperature can be functions of a parameter α, with $\gamma : x^i = x^i(\alpha); T = T(\alpha), \alpha_0 \leqslant \alpha \leqslant \alpha_1$.

If one considers a transformation which does not involve isothermal paths, then one can write $(\delta Q_{rev})_\gamma = C_\gamma \, dT$ along a path $\gamma(T)$ where deformation coordinates are functions of the temperature T, i.e. $\gamma : x^i = x^i(T), T_0 \leqslant T \leqslant T_1$, so that the line integral above becomes

$$\Delta S = \int_{T_0}^{T_1} \frac{dT}{T} C_\gamma(T) \tag{16}$$

where $C_\gamma(T)$ is assumed to be at least continuous and it is defined by

$$C_\gamma = \left(\frac{\delta Q_{rev}}{dT}\right)_\gamma = T \left(\frac{dS}{dT}\right)_\gamma$$

$$= T \left(\frac{\partial S}{\partial T}\right)_{x^i} + T \sum_i \left(\frac{\partial S}{\partial x^i}\right)_T \left(\frac{dx^i}{dT}\right)_\gamma. \tag{17}$$

See also [13], p 71, for the definition of the heat capacity along a generic path. Equation (16) represents an important tool in what follows.

It is also important to note that one can obtain generalized heat capacities in two modes. One can fix the curve $\gamma(T)$ and then calculate the corresponding heat capacity. One can also

fix a function $C(T)$ (at least continuous) and wonder if it is possible to find a path $\gamma(T)$ such that $C_\gamma(T) = C(T)$. The latter question has a positive answer at least locally and under rather general conditions. In fact, by fixing n functions $x^j(T)$ at least of class C^1 and by fixing a continuous function $C(T)$, the equality $C_\gamma(T) = C(T)$ can be considered as an ordinary differential equation in the remaining variable $x^i(T)$, and, given the corresponding Cauchy problem $x^i(0) = x_0^i$ one can find at least locally a solution. See also section 5.2, where this topic is explicitly treated in a special case. In the case of fixed deformation parameters one fixes the path and obtains $C_{x^1,\ldots,x^{n+1}}(T)$ which is a function related to the thermal stability properties of the system.

Note that the deformation parameters are assumed to be finite at $T = 0$; *a priori* this assumption is not necessary in order to get a finite entropy at $T = 0$ and it is implicit in the standard treatment of Nernst's heat theorem, but it is the case to make it explicit herein; cf [5], in particular the introduction and section IV therein. A discussion on this topic is given in section 8.

There can be a non-trivial violation of (F) above, which can occur when $T \to 0^+$ can be obtained as $U \to +\infty$. This topic is briefly discussed in appendix C.

4. (N) and differential criteria

As is well known, (N) is equivalent to the requirement that

$$\lim_{T \to 0^+} S(T, x^1, \ldots, x^{n+1}) = \Sigma_0 \tag{18}$$

where the value of the constant Σ_0 has to be zero in standard homogeneous thermodynamics [1]. We recall that, if (N) holds, then S is continuous at $T = 0$ (result 1 of [1]). In the following we consider Σ_0 as a constant with $0 \leqslant \Sigma_0 < +\infty$.

In the literature, it is assumed that (N) is equivalent to the requirement that the limit as $T \to 0^+$ of the partial derivatives of S with respect to deformation parameters vanishes,

$$\lim_{T \to 0^+} \left(\frac{\partial S}{\partial x^i} \right) (T, x^1, \ldots, x^{n+1}) = 0 \qquad \forall i = 1, \ldots, n+1 \tag{19}$$

for any choice of $x^1, \ldots, x^{n+1}$ [14]. We give here some mathematical details allowing us to see when differential conditions (19) are equivalent to (N).

4.1. (N) $\Rightarrow$ (19)

Result 1. *Let us assume* $S(T, x^1, \ldots, x^{n+1}) \in C^1(\mathcal{D} \cup \{T = 0\})$ *and that (N) holds. Then (19) follows.*

Proof. If (N) holds then $S(0, x^1, \ldots, x^{n+1}) \equiv \Sigma(x^1, \ldots, x^{n+1})$ is constant. This means that $\mathrm{d}\Sigma = 0$ for any point $(0, x^1, \ldots, x^{n+1})$ contained in the surface $T = 0$. If $\phi : \mathcal{D} \cup \{T = 0\} \to \{T = 0\}$ is the regular map such that $T, x^1, \ldots, x^{n+1} \mapsto 0, x^1, \ldots, x^{n+1}$, then one has $\Sigma(x^1, \ldots, x^{n+1}) = S \circ \phi = \phi^* S$, where ϕ^* is the corresponding pullback map. As a consequence, one has $\phi^*(\mathrm{d}S) = \mathrm{d}(\phi^* S) = \mathrm{d}\Sigma$ (for simplicity, the same symbol d is used for the differential in the whole domain and the differential restricted to the surface $T = 0$). Then, for all $i = 1, \ldots, n+1$ it holds that

$$\left(\frac{\partial S}{\partial x^i} \right)_{T=0} = \frac{\partial \Sigma}{\partial x^i}. \tag{20}$$

Having S of class C^1, by continuity one finds

$$\lim_{T \to 0^+} \left(\frac{\partial S}{\partial x^i} \right) = \frac{\partial \Sigma}{\partial x^i}. \tag{21}$$

Equation (19) is then a consequence of $d\Sigma = 0$, which holds if (N) holds under the above hypotheses. □

One can also allow a more general setting. We define, for simplicity of notation, by $L^1(\mathcal{U}_+(0))$ the space of the functions $f(T, x^1, \dots, x^{n+1})$ which are integrable in a right neighbourhood $\mathcal{U}_+(0)$ of $T = 0$ for all $x^1, \dots, x^{n+1}$ (in the sense that there exists a function $m(T) \in L^1((0, T_0])$ such that $|f(T, x^1, \dots, x^{n+1})| < m(T)$ for all $x^1, \dots, x^{n+1}$) and whose (maybe improper) integral in dT over the interval $(0, T]$ gives rise to a function of $T, x^1, \dots, x^{n+1}$ which is continuous also at $T = 0$. The latter property can, e.g., be ensured as in the discussion in appendix B of [1].

We assume the following properties:

$$a_0 \equiv \partial S / \partial T = \frac{C_{x^1, \dots, x^{n+1}}(T)}{T} \in L^1(\mathcal{U}_+(0)) \cap C(\mathcal{D}) \tag{22}$$

$$a_i \equiv \partial S / \partial x^i \in C(\mathcal{D} \cup \{T = 0\}) \qquad \forall i = 1, \dots, n+1. \tag{23}$$

Note that (22) allows also $\partial S / \partial T \to \infty$ in the limit of vanishing temperature[3]. We introduce the following definition. A set $\Omega \subset \mathbb{R}^k$ has the *polygonal property* if for any couple of points $\vec{x}_0, \vec{x}_1 \in \Omega$, there exists a polygonal curve which joins $\vec{x}_0$ and $\vec{x}_1$ and which is piecewise parallel to the coordinate axes. By assuming that the domain $\mathcal{D} \cup \{T = 0\}$ has the polygonal property and by using, e.g., variables T, x, y without loss of generality, one can write

$$S(T, x, y) - S(T, x_0, y_0) = \int_{x_0}^{x} dz \, a_1(T, z, y_0) + \int_{y_0}^{y} dz \, a_2(T, x, z). \tag{24}$$

The following result holds:

Result 2. *Let us assume that the domain $\mathcal{D} \cup \{T = 0\}$ has the polygonal property and that (N), (22) and (23) hold. Then (19) follows.*

Proof. By using variables T, x, y without loss of generality, (N) implies that the right member of (24) vanishes in the limit as $T \to 0^+$. The arbitrariness of $x_0, x; y_0, y$ implies that

$$\lim_{T \to 0^+} \int_{x_0}^{x} dz \, a_1(T, z, y_0) = 0 \tag{25}$$

$$\lim_{T \to 0^+} \int_{y_0}^{y} dz \, a_2(T, x, z) = 0 \tag{26}$$

(one could choose $y = y_0$ and then choose $x = x_0$); the continuity of the integrals [15] allows us to write

$$\lim_{T \to 0^+} \int_{x_0}^{x} dz \, a_1(T, z, y) = \int_{x_0}^{x} dz \lim_{T \to 0^+} a_1(T, z, y) \tag{27}$$

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[3] If $\lim_{T \to 0^+}(\partial S / \partial T)$ exists and is finite and (23) is satisfied, one has that S can be formally extended in such a way that $S \in C^1(\mathcal{D} \cup \{T = 0\})$. If $\partial S / \partial T \to \infty$ is allowed, one has a behaviour similar to that of second-order phase transitions, where $(\partial S / \partial T) \to +\infty$ as $T \to T_c$; but the latter divergence corresponds to a divergence in the heat capacity; instead, as $T \to 0^+$, one has a vanishing heat capacity.

and the same is true for the integral of $a_2(T, x, y)$. Then (N) implies that

$$\lim_{T \to 0^+} a_1(T, x, y) = 0 \tag{28}$$

$$\lim_{T \to 0^+} a_2(T, x, y) = 0. \tag{29}$$

In fact, let $a_1(0, \bar{x}, \bar{y}) > 0$. Then, in a neighbourhood $A(0, \bar{x}, \bar{y})$ of $(0, \bar{x}, \bar{y})$ the function a_1 is positive by continuity. If $A \ni \bar{x}_0 < \bar{x}$, the function $a_1(0, x, \bar{y})$, with $x \in [\bar{x}_0, \bar{x}]$ and $\bar{y}$ fixed, is positive and continuous in x and $\min_{x \in [\bar{x}_0, \bar{x}]} a_1(0, x, \bar{y}) \equiv m > 0$. Then $\int_{\bar{x}_0}^{\bar{x}} \mathrm{d}z \, a_1(0, z, \bar{y}) \geqslant m(\bar{x} - \bar{x}_0) > 0$, against (25). If $a_1(0, \bar{x}, \bar{y}) < 0$ the proof is analogous. $\qquad\square$

Summarizing, (N) implies that (19) holds, i.e. all the coefficients of $\mathrm{d}S_\perp$ vanish as $T \to 0^+$.

4.2. (19) ⇒ (N)

The converse implication is summarized in

Result 3. *Let us consider $\mathcal{D} \cup \{T = 0\}$ having the polygonal property and such that $T^{-1}(0)$ is connected; Let*

$$\mathrm{d}\mathcal{B} \equiv b_0(T, x^1, \ldots, x^{n+1}) \, \mathrm{d}T + \sum_{i=1}^{n+1} b_i(T, x^1, \ldots, x^{n+1}) \, \mathrm{d}x^i \tag{30}$$

be an exact continuous differential form on $\mathcal{D}$ such that the following conditions hold,

$$\begin{aligned} b_0(T, x^1, \ldots, x^{n+1}) &\in \mathrm{L}^1(\mathcal{U}_+(0)) \cap C(\mathcal{D}) \\ b_i(T, x^1, \ldots, x^{n+1}) &\in C(\mathcal{D} \cup \{T = 0\}) \end{aligned} \tag{31}$$

and

$$\lim_{T \to 0^+} b_i(T, x^1, \ldots, x^{n+1}) = 0 \qquad \forall i = 1, \ldots, n+1 \tag{32}$$

Then

$$\mathcal{B}(T, x^1, \ldots, x^{n+1}) = \mathcal{B}_0 + \int_0^T \mathrm{d}z \, b_0(z, x^1, \ldots, x^{n+1}) \tag{33}$$

where $\mathcal{B}_0$ is a constant.

Proof. The proof is trivial. One has that $\mathcal{B}(T, x^1, \ldots, x^{n+1}) - \mathcal{B}(T, \bar{x}^1, \ldots, \bar{x}^{n+1})$ can be expressed in terms of integrals with respect to $\mathrm{d}x^i$ of $b_i(T, x^1, \ldots, x^{n+1})$. The continuity of the integrals then implies the thesis. $\qquad\square$

Note that these conditions are *not* rigorously equivalent to (N) as it has to be implemented in standard thermodynamics, because they still allow transformations $\gamma^0(T)$ starting from $T = 0$ with non-positive heat capacity $C_{\gamma^0}(T) \leqslant 0$. The stability condition of thermodynamics $C_{x^1, \ldots, x^{n+1}}(T) > 0$ amounts to $b_0(T, x^1, \ldots, x^{n+1}) > 0$ for $T > 0$ and forces also the non-existence of curves starting from $T = 0$ with negative heat capacity $C_{\gamma^0}(T) < 0$. See section 5.1.

Moreover, these differential criteria allow us to find that S is constant on each connected component of the surface $T = 0$. For a homogeneous system, $\lim_{T \to 0^+} S \equiv \Sigma_0 = 0$ and one cannot find two different values of Σ_0 on disconnected branches. If the system is non-homogeneous, one could *a priori* find two different entropy constants on two different branches, in agreement with [2].

In our discussion above, we have automatically excluded a behaviour analogous to Wheeler's counter-example (cf also [10]), where an isentrope reaching $T = 0$ exists and (N) is satisfied (obviously, the standard (U) is violated). This counter-example is involved with a violation of $C_{x^1,\ldots,x^{n+1}}(T) > 0$, as realized in [5]: indeed, it occurs because $C_p = 0$ on an interval $(0, T_1)$ [5]. Moreover, a pathological behaviour for the model is due to the fact that $S = 0$ is reached at $T > 0$, which can be considered pathological because of our reasoning in section 5.4.2 of [1].

It is interesting to see what happens in homogeneous thermodynamics by using extensive coordinates $B, X^1, \ldots, X^{n+1}$ in the Gibbs frame. One has $S = S(B, X^1, \ldots, X^{n+1})$. We have

$$\frac{\partial S}{\partial B} = \frac{1}{T(B, X^1, \ldots, X^{n+1})} \tag{34}$$

and

$$\frac{\partial S}{\partial X^i} = -\frac{\tilde{\xi}_i(B, X^1, \ldots, X^{n+1})}{T(B, X^1, \ldots, X^{n+1})} \tag{35}$$

where, by hypothesis, $\tilde{\xi}_i(B, X^1, \ldots, X^{n+1})$ are continuous functions for all $i = 1, \ldots, n+1$ also at the surface $T = 0$ and vanish there [1]. Condition (22) is replaced by the requirement that $1/T$ is integrable near $B = 0$ and $\int dB/T$ gives rise to a continuous function (see [1]). If $\partial S/\partial X^i = -\tilde{\xi}_i(B, X^1, \ldots, X^{n+1})/T(B, X^1, \ldots, X^{n+1}) \to 0$ as $B \to 0^+$, in such a way that $\tilde{\xi}_i/T$ is continuous also for $B = 0$, then one can again take the limit as $B \to 0^+$ within the integral $\int dX^i \tilde{\xi}_i/T$, and then (N) holds.

Note also that the latter considerations hold true also in non-homogeneous thermodynamics in the Gibbs-like framework sketched in section 2.2, if the analogous B coordinate can be defined.

4.3. Counter-examples against a too naive use of the differential criteria

It is remarkable that, if one relaxes (23) for the entropy, then (N) can hold even if condition (19) is violated. We give an example in the following, in which we focus on mathematics rather than on physical meaning. A toy model can be as follows,

$$S(T, V, M) = T(V + c\sqrt{VM}) \tag{36}$$

where M is an extensive variable such that $M \geqslant 0$, $V > V_0 > 0$ and c is a constant. One can, e.g., think that M is the magnetization. One finds

$$\frac{C_{VM}}{T} = V + c\sqrt{VM}$$

$$\frac{\partial S}{\partial V} = T\left(1 + \frac{c}{2}\sqrt{\frac{M}{V}}\right) \tag{37}$$

$$\frac{\partial S}{\partial M} = T\frac{c}{2}\sqrt{\frac{V}{M}}$$

the partial derivative $\partial S/\partial M$ diverges in the limit as $M \to 0$ and it is not continuous in $(0, V, 0)$. There is no contradiction with the previous discussion, in fact in the above example condition (23) is clearly violated, even if only on a zero measure set. This is an interesting signal that the failure of (19) does not automatically mean that (N) is violated. Equation (19) is a stronger condition (required, e.g., in [14]). An example of this kind of behaviour for random spin systems is given in [16], where (N) is preserved and (19) is violated because of the non-vanishing of $\partial \chi/\partial T$ (χ is the susceptibility) for $T \to 0^+$ and the magnetic field $H \to 0$.

5. Condition (Π)

We introduce here a condition which is equivalent to (N). This condition involves a discussion of the sign of the heat capacity along a generic transformation in a neighbourhood of $T = 0$. *A priori*, it is not necessary that the heat capacity along a generic transformation is positive. The presence of $C_\gamma < 0$ in standard thermodynamics does not contradict the concavity property of the entropy, which requires that the heat capacity along transformations at constant deformation parameters is positive. Along generic transformations at non-constant deformation parameters, the heat capacity can be negative without violating any stability criterion. One can consider, e.g., the polytropic transformations $T V^{z-1} = $ const of an ideal gas, whose specific heat is negative when the polytropic index z is strictly contained in the interval $(1, c_p/c_v)$ [2]. As is known, ideal gases satisfy stability criteria.

We introduce the following condition, which is shown to be equivalent to (N):

Condition (Π). *For any point $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ belonging to the surface $T = 0$ and for any reversible transformation $\gamma^0(T)$ which is parametrized by T and starts at $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$, the heat capacity $C_{\gamma^0}(T)$, which is assumed to be a continuous function of T and such that $C_{\gamma^0}(T)/T$ is integrable near $T = 0$, becomes positive in the limit as $T \to 0^+$, i.e. there exists a neighbourhood $(0, T_\epsilon(\gamma^0))$ where $C_{\gamma^0}(T) > 0$ and*

$$\lim_{T \to 0^+} C_{\gamma^0}(T) = 0^+. \tag{38}$$

We note that $T_\epsilon(\gamma^0)$ depends in general on the curve γ^0 connected to $T = 0$; the integrability of $C_{\gamma^0}(T)/T$ is imposed in order to obtain a finite entropy at $T = 0$. Then, integrability implies that $C_{\gamma^0}(T) \to 0$ as $T \to 0$ has to hold, and the latter condition is much weaker than (38).

Condition (Π) can be considered natural in standard thermodynamics, because it matches, at least near $T = 0$, the condition of positivity for heat capacities in transformations at constant deformation parameters. This condition, to some extent, corresponds to the original proposal of Nernst. In fact, Nernst also linked his heat theorem to the vanishing of the heat capacities as $T \to 0^+$ [17] (cf also [18]). Actually, the condition to be imposed is (Π), which is much stronger than the simple vanishing of the heat capacities at constant deformation parameters as $T \to 0^+$, and requires, in order to ensure (N), some further topological condition. Note also that it is assumed that $\gamma^0(T)$ does not contain any isothermal sub-path in order to get a well-defined heat capacity; this restriction does not imply a loss of generality, because we are interested in the behaviour of paths leaving the surface $T = 0$. Moreover, it is not necessary that $C_{\gamma^0}(T) > 0$ holds for any finite $T > 0$ (which would be, in general, false), it simply requires that, near $T = 0$, all heat capacities along curves connected to $T = 0$ become positive. A detailed discussion is found in the following subsections. Note also that this condition forbids the existence of the isentropic transformations allowing $T = 0$ to be reached (for these transformations it holds that $C_{\gamma^0}(T) = 0$).

5.1. Condition (Π) versus (N)

We start by discussing the relation between (N) and condition (Π); we show that (N) $\Leftrightarrow$ (Π). We work in a framework where homogeneity can be removed. A relevant role is played by the stability condition, the validity of (39) everywhere and also the existence for each point $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ belonging to the surface $T = 0$ of a rectangular neighbourhood $[0, T_0] \times I_1 \times \cdots \times I_{n+1}$, where I_i is an interval for each $i = 1, \ldots, n + 1$ and $\left(x_0^1, \ldots, x_0^{n+1}\right)$

is an inner point of $I_1 \times \cdots \times I_{n+1}$.[4] Note also that, in the standard homogeneous case as realized in section 2.1, these conditions are implemented.

5.1.1. (N) $\Rightarrow$ (Π).   We begin from the easy part of the double implication:

Result 4. *Let us assume that $S \in C^1(\mathcal{D})$ and that*

$$S(T, x^1, \ldots, x^{n+1}) = \Sigma_0 + \int_0^T \frac{dz}{z} C_{x^1, \ldots, x^{n+1}}(z) \tag{39}$$

holds in $\mathcal{D}$. Moreover, let us assume the thermal stability property

$$C_{x^1, \ldots, x^{n+1}}(T) > 0 \qquad \forall T > 0 \quad and \quad \forall x^1, \ldots, x^{n+1}. \tag{40}$$

Then (Π) holds.

Proof. For any choice of $T, x^1, \ldots, x^{n+1}$ one has

$$S(T, x^1, \ldots, x^{n+1}) \geqslant \Sigma_0 \tag{41}$$

and

$$S(T, x^1, \ldots, x^{n+1}) > \Sigma_0 \qquad \forall T > 0 \quad and \quad \forall x^1, \ldots, x^{n+1} \in \mathcal{D}. \tag{42}$$

As a consequence, there is no (piecewise C^1) oriented simple curve γ^0 in $\mathcal{D}$ reaching $T = 0$ such that $C_{\gamma^0} \leqslant 0$ in a right neighbourhood of absolute zero, because, contrarily, one should have for $T > 0$ sufficiently near $T = 0$

$$S(\gamma^0(T)) = \Sigma_0 - \int_0^T \frac{dz}{z} |C_{\gamma^0}(z)| < \Sigma_0 \tag{43}$$

which is impossible because of (42). At the same time, an isentrope $C_{\gamma^0} = 0$ connected to $T = 0$ is also impossible, because of (42). $\square$

For the case where (N) holds with $\Sigma_0 = 0$, one can also remove the assumption of the validity of the formula (39) everywhere. In fact, S gets its absolute minimum $S = 0$ at $T = 0$ and $S = 0$ cannot be allowed elsewhere (cf [1] for the homogeneous case). Then, from

$$S(\gamma^0(T)) = \int_0^T \frac{dz}{z} C_{\gamma^0}(z) > 0 \tag{44}$$

one finds that (Π) has to hold. The requirement for the validity of (40) can also be limited to $T \in (0, T_\epsilon)$. This condition means that S is a strictly monotonically increasing function of T for $T \in (0, T_\epsilon)$. Then one finds that (43) is impossible and that an adiabatic reversible transformation $C_{\gamma^0} = 0$ reaching $T = 0$ cannot occur, and, moreover, that $S(T, x^1, \ldots, x^{n+1}) > \Sigma_0$ for all $T \in (0, T_\epsilon)$ and for all $x^1, \ldots, x^{n+1}$.

5.1.2. The hard part: (Π) $\Rightarrow$ (N).   We preliminarily point out that the non-existence of a γ^0 such that $C_{\gamma^0} < 0$ is a necessary condition for the validity of (N) in the case of a homogeneous system with $S \geqslant 0$. In fact, let us assume that such a curve exists; then, one has

$$S(T, x^1(T), \ldots, x^{n+1}(T)) = \int_0^T \frac{dz}{z} C_{\gamma^0}(z) + S(0, x_0^1, \ldots, x_0^{n+1}) < S(0, x_0^1, \ldots, x_0^{n+1}). \tag{45}$$

Then, one surely has $S(0, x_0^1, \ldots, x_0^{n+1}) > 0$. Because of the homogeneity, the entropy $S(0, x_0^1, \ldots, x_0^{n+1}) > 0$ cannot be a constant independent of the deformation parameters

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[4] This can be obtained, e.g., if there exists a neighbourhood of the form $[0, T_0) \times W_0$ where $W_0 \subset \mathbb{R}^{n+1}$ is a spherical neighbourhood centred in $(x_0^1, \ldots, x_0^{n+1})$.

$x^1, \ldots, x^{n+1}$ (or such a constant should be zero). As a consequence (N) has to be violated and the range of S at $T = 0$ is an interval. One could still allow a single isentrope $S = 0$ to reach $T = 0$. But we consider such behaviour as pathological, and, moreover, impossible if a strict concavity $C_{x^1, \ldots, x^{n+1}}(T) > 0$ for $T > 0$ holds (and also when (1) is assumed; cf [1]).

As far as the thermal stability condition is concerned, we show in the following subsection that it is not a necessary condition to be required with (Π) in order to obtain (N). Nevertheless, it holds in homogeneous thermodynamics and it allows us to obtain a simple proof of the above implication. Note also that (Π) has to hold also for constant deformation coordinates, which implies that, for any fixed $x_0^1, \ldots, x_0^{n+1}$, there exists a $T_\epsilon(x_0^1, \ldots, x_0^{n+1}) > 0$ such that $C_{x_0^1, \ldots, x_0^{n+1}}(T) > 0$ in $\left(0, T_\epsilon(x_0^1, \ldots, x_0^{n+1})\right)$ (a sort of 'ultra-local' stability condition). We do not use this condition herein, we limit ourselves to point out that in the following proof the stability condition (40) can be replaced by $C_{x^1, \ldots, x^{n+1}}(T) > 0$ for all $T \in (0, T_\epsilon)$ and for all $x^1, \ldots, x^{n+1}$.

Result 5. *Let us assume the following: $S \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$; condition (Π) holds; the stability condition (40) holds; $\{T = 0\}$ is connected and any point at $T = 0$ has a rectangular neighbourhood. Then (N) follows.*

Proof. We show that a violation of (N) implies a violation of (Π). Let us assume that (N) is violated. We point out that if $T = 0$ is not connected, the following considerations hold for each connected component of $T = 0$ where S is not constant. Then in (the aforementioned connected component of) $T = 0$ there exists $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ which is not a local minimum for S. In fact, the range of $\Sigma\left(x_0^1, \ldots, x_0^{n+1}\right) \equiv S\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ is an interval (Σ_0, Σ_1) and it is easy to show that this implies that there are points which are not local minima for S. We sketch the proof in appendix D.

From the analysis carried out in [1], we know that in standard thermodynamics, if (N) is violated, there exists an isentropic surface reaching $T = 0$. In a more general setting, one can introduce $\sigma_0(T, x^1, \ldots, x^{n+1}) \equiv S(T, x^1, \ldots, x^{n+1}) - S\left(0, x_0^1, \ldots, x_0^{n+1}\right)$, which is a continuous function monotonically strictly increasing in T because of $C_{x^1, \ldots, x^{n+1}}(T) > 0$. A variant of the implicit function theorem, which can be implemented by following step by step, with obvious changes, the proof in section 5.6 of [1], shows that, if $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ is not a local minimum for S, there exists a unique continuous function $T(x^1, \ldots, x^{n+1})$ such that $\sigma_0(T(x^1, \ldots, x^{n+1}), x^1, \ldots, x^{n+1}) = 0$ in a neighbourhood of $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ and such that $T\left(x_0^1, \ldots, x_0^{n+1}\right) = 0$. Then, such a surface allows the existence of curves reaching $T = 0$ with $C_{\gamma^0} = 0$. As a consequence, (Π) is violated. $\square$

Note that the topological condition to be satisfied in order to give meaning to condition (Π) consists in the possibility of accessing points at $T > 0$ from $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$. This condition is trivially satisfied if the domain is convex, because any inner point can be reached from any other point belonging to the boundary $T = 0$ along segments. By relaxing convexity of the domain, one can still obtain this property by requiring that each point of the boundary has a rectangular neighbourhood (sufficient condition). Contrarily, it is easy to construct a counter-example where (Π) holds but (N) is violated (e.g., consider a continuous $S(T, x)$ such that $S(0, x) = x$ for $x \in (x_0, x_1)$ and $S(T, x) = Tx + S_0$ for $x \geqslant x_1$ and for $T > 0$, with $S_0 = x_1$). But states $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ from which it is not possible to reach directly other states at $T > 0$ are not allowed in our hypotheses (they seem to be also unphysical).

One could object that the requirement for S to get a constant value at the hypersurface $T = 0$ could be satisfied even by allowing $C_{\gamma^0} < 0$. Note again that this objection cannot be applied to the homogeneous case because $S = 0$ is necessarily a global minimum for S. Moreover, stability condition $C_{x^1, \ldots, x^{n+1}}(T) > 0$ does not allow, even in a non-homogeneous

case, to reach values $S(T, x^1, \ldots, x^{n+1}) < \Sigma_0$, where Σ_0 is the entropy constant at $T = 0$ (cf equation (39)). By relaxing both $C_{x^1,\ldots,x^{n+1}}(T) > 0$ (at least near $T = 0$) and homogeneity, the toy-model function $S(T, x) : [0, T_1) \times (x_0, x_2) \to \mathbb{R}$, defined by $S(T, x) = T(x_1 - x) + \Sigma_0$, where $x_2 > x_1 > x_0$ and $\Sigma_0 \geqslant T_1(x_2 - x_1)$ is a non-negative constant, satisfies (N) and allows a violation of (Π) for $x_1 \leqslant x < x_2$.

5.2. Condition (Π) and differential equations

We show that the theory of ordinary differential equations can be used in order to show that a violation of (N) implies a violation of (Π) and in order to find the relation with differential conditions. Moreover, we show that the stability condition is not essential in order to show that $(\Pi) \Rightarrow (N)$. We assume that (22) and (23) hold. Herein, the existence of a rectangular neighbourhood for points belonging to $T = 0$ matches the hypotheses of existence theorems for solutions of ordinary differential equations used in the following. Our main result is

Result 6. *Let us assume the following: condition (Π) holds; (23) and (22) hold; $\{T = 0\}$ is connected and any point at $T = 0$ has a rectangular neighbourhood. Then (N) follows.*

Proof. Let us introduce $\vec{n} \equiv (\mathrm{d}x^1/\mathrm{d}T, \ldots, \mathrm{d}x^{n+1}/\mathrm{d}T)$ and $\vec{\nabla}S \equiv (\partial S/\partial x^1, \ldots, \partial S/\partial x^{n+1})$. Then, we have

$$\frac{\mathrm{d}S}{\mathrm{d}T} = \frac{\partial S}{\partial T} + \vec{n} \cdot \vec{\nabla}S. \tag{46}$$

Condition (Π) requires that

$$T\frac{\mathrm{d}S}{\mathrm{d}T} \to 0^+ \quad \text{as} \quad T \to 0^+ \tag{47}$$

whichever path starting from $T = 0$ is chosen. One finds

$$\frac{T\,\mathrm{d}S/\mathrm{d}T}{T\,\partial S/\partial T} = 1 + (\vec{n} \cdot \vec{\nabla}S)\frac{1}{\partial S/\partial T}. \tag{48}$$

(Π) can be implemented only if $\vec{\nabla}S \to 0$, and this implies that (N) has to hold. In fact, let us assume, e.g., that $\partial S/\partial x^1$ does not vanish as $T = 0$ is approached, which means that (N) is violated, and let us keep all the other x^j fixed. Then, if $\eta(T) \in L^1((0, T_0])$ is a negative definite function such that

$$C_{\gamma^0}(T) \equiv T\eta(T) \tag{49}$$

by choosing

$$n_1 = -\frac{1}{\partial S/\partial x^1}(|\eta(T)| + \partial S/\partial T) \equiv h(T, x) \tag{50}$$

condition (Π) can be violated. Equation (50) is a differential equation ($n_1 = \mathrm{d}x^1/\mathrm{d}T$ by definition) and a Cauchy problem with initial condition $x^1(0) = x_0^1$ can be defined. Under the hypotheses (22), (23) one finds that $h(T, x)$ is a measurable function satisfying the hypotheses of the Carathéodory theorem on ordinary differential equations [19] (even the conditions of the Peano theorem if $\partial S/\partial T$ and $\eta(T)$ are continuous functions at $T = 0$), thus a local solution exists for the corresponding Cauchy problem with initial point $x^1(0) = x_0^1$ such that $\partial S/\partial x^1(0, x_0^1, \ldots, x_0^{n+1}) \neq 0$, against condition ($\Pi$). The same is true in the more general setting where $x^j(T) \in C^1([0, T_1])$ for $j \neq 1$ are fixed functions. Also isentropes reaching $T = 0$ can be found (by putting $\eta = 0$) if (N) is violated. $\qquad\square$

Under our hypotheses, the condition $\partial S/\partial x^1(0, x_0^1, \ldots, x_0^{n+1}) \neq 0$ means that $(0, x_0^1, \ldots, x_0^{n+1})$ is not a local minimum for S. As an (maybe oversimplified but still

meaningful) example of the relevance of the condition for $\left(0, x_0^1, \ldots, x_0^{n+1}\right)$ not to be a local minimum in order to solve the Cauchy problem, let us consider $S(T, x) = cT + (x - x_0)^2$, with $c > 0$ and $x, x_0 > 0$. It is evident that $(0, x_0)$ is the absolute minimum of S. One has $\partial S/\partial x = 2(x - x_0)$ and $\partial S/\partial T = c > 0$. Let us choose $\eta(T) = -1$. Then, let us consider the Cauchy problem

$$\left(\frac{\mathrm{d}x}{\mathrm{d}T}\right) = -\frac{1}{2(x - x_0)}(1 + c) \qquad x(0) = x_1. \tag{51}$$

If, e.g., $x_1 > x_0$, then $x(T) = x_0 + \sqrt{(x_1 - x_0)^2 - (1 + c)T}$ solves the problem (51) for $0 \leqslant T \leqslant (x_1 - x_0)^2/(1 + c)$; if, instead, $x(0) = x_0$, then $\partial S/\partial x$ vanishes as $x \to x_0$ and there is no solution of the Cauchy problem (51).

We point out that, if (N) holds, the equation $C_{\gamma^0}(T) = 0$ cannot have solutions where all the $x^i(T)$ are finite in the limit as $T \to 0^+$; cf section 5.6 in [1].

We find that a violation of (N) implies a violation of (Π), with no reference to the thermal stability condition.

It can also be noted that, if thermal stability is violated, then (N) can still hold if $\vec{\nabla} S$ vanishes as $T \to 0^+$ (see result 3), but (Π) is violated and $(N) \not\Rightarrow (\Pi)$.

5.3. Condition (Π) and heat

A comment about the meaning of condition (Π) in terms of the heat that the system can exchange is in order. Condition (Π) implies that, for any curve γ^0 connected to $T = 0$, there is a right neighbourhood $[0, T_\epsilon(\gamma^0))$ of absolute zero such that $C_{\gamma^0}(T) > 0$. Then in the same neighbourhood

$$Q_{\gamma^0} = \int_0^{T_\epsilon(\gamma^0)} \mathrm{d}T \, C_{\gamma^0}(T) > 0. \tag{52}$$

As a consequence, in order to leave the surface $T = 0$ it is necessary to supply heat to the system, whichever reversible transformation is chosen in the thermodynamic space. (Note that, for any $T_\epsilon > 0$, no matter how near $T = 0$, there exists the possibility of extracting heat from the system along the isotherm $T = T_\epsilon$. Thus, it would be incorrect to say that there exists a right neighbourhood of $T = 0$ where heat cannot be extracted from the system.) We have also shown that, if (N) is violated, under suitable hypotheses it is, in principle, possible to get $C_{\gamma^0}(T) < 0$.

According to the first law,

$$\Delta U_{\gamma^0} = Q_{\gamma^0} - W_{\gamma^0} \tag{53}$$

the system can transfer energy via the macroscopically observable modes of motion (work term W) and via the hidden atomic modes of motion (heat term Q) [20]. The extraction of energy by means of heat $Q_\gamma < 0$ implies the subtraction of energy as an effect of microscopic 'disordered' interactions of the system with its environment[5]. As a consequence of condition (Π), the hidden atomic modes of motion can allow only a transfer of energy into the system if one starts from $T = 0$. This fact could be interpreted by saying that hidden atomic modes of motion are frozen at $T = 0$ and that an hindrance against any extraction of heat from the system occurs if a state at $T = 0$ has to be left, as is to some extent natural

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[5] In, e.g., [21], the process of heat flow is described in microscopic terms as a 'diffusive' energy release, by means of microscopic molecular collisions, between nearby regions and at the interface system–environment. Heat could be naively interpreted also as mean microscopic 'disordered' work associated with molecular collisions, which should represent the mean 'disordered' work contribution of hidden microscopic modes of motion.

and expected: there is no 'thermal motion' at absolute zero and one has to supply heat to the system in order to 'turn on' hidden atomic modes of motion and in order to reach a state at $T > 0$.

The violation of (N), instead, would imply that heat can be extracted from a system when it leaves a state at $T = 0$, that is, some microscopic degrees of freedom should still be able to release energy via hidden modes of motion without any previous heat supply to the system. Moreover, states at $T > 0$ could also be reached adiabatically; because of the peculiar nature of the surface $T = 0$ to be an adiabatic surface, adiabatic inaccessibility would be jeopardized by the intersection of the aforementioned adiabatic and non-isentropic surface $T = 0$ and isentropic surfaces occurring at $T > 0$ [1].

The aforementioned release of heat could be plausible in the case of glassy substances (for details on this topic see, e.g., [13, 22, 23]), where there are frozen non-equilibrium states which could be implied in such a heat release. It is to be noted, however, that glassy substances, and, in general, phenomena which would imply a violation of the third law because of 'frozen-in disorder' at $T = 0$ [13], actually violate Gibbs' requirement of "balance of the active tendencies of the system" (quoted from [13]) for equilibrium states (they are actually characterized by non-equilibrium states in which "passive forces or resistances to change" [13] appear), so that no true violation of the third law appears. However, on this topic there is controversy, an opposite opinion is expressed, e.g., in [23] and also in [24], section 61b. We wish also to recall that the third law $\lim_{T \to 0^+} S = 0$ has been assumed as a fundamental operational criterion for the definition of 'equilibrium state' by Tisza [25]. In general, it is not hard to figure a 'release of energy from systems at $T = 0$' where the energy is released by means of a 'disordered microscopic transfer mechanism' (heat). One could, e.g., consider a statistical ensemble at $T = 0$ of radioactive nuclei decaying with the appropriate statistical law; the corresponding decays could give rise to a release of energy which could be considered 'heat' (in fact it is associated with 'collisional work'). It is to be noted that the transformation is irreversible and also that the initial state cannot be considered as a true equilibrium state according to the definition by Gibbs (it is associated with an intrinsic instability). Anyway, exotic thermodynamics could also be involved in a violation of (Π) and of (N) without invoking frozen-in disorder[6]. (For such an exotic thermodynamics, one could also introduce the opposite of condition (Π) for ensuring (N), i.e. the requirement that $C_{\gamma^0}(T) < 0$ for $T \in (0, T_\epsilon(\gamma^0))$ for all $\gamma^0(T)$. Changes in the previous proofs are obvious).

Summarizing, we can rephrase the third law also as follows:

For any physical system it is impossible to leave a thermodynamic equilibrium state belonging to the surface $T = 0$ without heat absorption, whichever reversible transformation $\gamma^0(T)$ starting at $T = 0$ is considered.

In the latter version, the third law is again stated in the form of a 'law of impotence' [24] as in its standard unattainability version (U). Note also that the aforementioned impossibility, according to condition (Π), implies the impossibility of performing an adiabatic reversible path reaching $T = 0$.

5.4. A geometrical characterization of condition (Π)

The heat capacity along a generic curve is simply the contraction of the differential form δQ_{rev} with the tangent vector $\dot{\gamma}$ along the generic thermodynamic transformation γ; the preferred parameter for γ is the temperature T, but there is no problem if a generic parametrization

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[6] In black hole thermodynamics, the violation of (N) is evident and 'subtraction of heat from $T = 0$' is, in principle, possible; there is no definitive indication about the microscopic degrees of freedom involved.

is assumed. In fact, a change in parametrization amounts simply to considering $T = T(\tau)$, where τ is a new parameter. By starting at $T = 0$, it is natural to get $T(\tau)$ as an increasing function. The Pfaffian form $\delta Q_{\text{rev}} = dU - \sum_i \xi_i \, dx^i$ under the map $U \mapsto T$ becomes

$$\delta Q_{\text{rev}} = \frac{\partial U}{\partial T} \, dT + \sum_i \left(\frac{\partial U}{\partial x^i} - \xi_i \right) dx^i$$

$$= C_{x^1,\dots,x^{n+1}}(T) \, dT + \sum_i T \left(\frac{\partial S}{\partial x^i} \right) dx^i. \tag{54}$$

The tangent vector $\dot{\gamma}$ can be written as

$$\dot{\gamma} = \partial_T + \sum_i \frac{dx^i}{dT} \partial_{x^i}. \tag{55}$$

By contracting $\dot{\gamma}$ with δQ_{rev} one obtains

$$\delta Q_{\text{rev}}(\dot{\gamma}) = C_{x^1,\dots,x^{n+1}}(T) + \sum_i T \left(\frac{\partial S}{\partial x^i} \right) \frac{dx^i}{dT} \tag{56}$$

which is, obviously, coincident with

$$\left(\frac{\delta Q_{\text{rev}}}{dT} \right)_{\text{along } \gamma}. \tag{57}$$

As a consequence, it coincides with the heat capacity along the given curve: $C_\gamma(T) = \delta Q_{\text{rev}}[(\dot{\gamma})]$. Condition ($\Pi$) requires that $\lim_{T \to 0^+} \delta Q_{\text{rev}}[(\dot{\gamma}^0)] = 0^+$. It is evident that (N) implies that the entropy S can only increase in leaving $T = 0$ and that one can only furnish heat to the system in order to perform such an operation. The converse is also true, as we have shown in the previous section.

6. Condition (Π) in the Gibbsian frame

Let us consider the frame where $B, X^1, \dots, X^{n+1}$ are the independent coordinates of the thermodynamic space, both in homogeneous thermodynamics and in non-homogeneous thermodynamics. Given a simple oriented C^1 curve $\gamma(\tau) : [0, 1] \to \mathcal{D}$ and its tangent vector

$$Z \equiv \frac{dB}{d\tau} \partial_B + \sum_i \frac{dX^i}{d\tau} \partial_{X^i} \tag{58}$$

one can define the (at least continuous) function

$$K_\gamma(\tau) = \delta Q_{\text{rev}}(Z) \tag{59}$$

which is such that

$$S(\gamma(\tau)) = S(\gamma(0)) + \int_0^\tau d\tau \, \frac{K_\gamma(\tau)}{T(\tau)}. \tag{60}$$

K_γ plays a role analogous to the role of C_γ in (16). It is useful to use B as a curve parameter (one can also use a parameter $\tau \in [0, 1]$ with $(dB/d\tau) > 0$ and $B(\tau = 0) = 0$ if a curve starting from a state at $T = 0$ is considered; what follows holds true). Then, given a curve $\gamma(B)$, we find its tangent vector

$$Z_B = \partial_B + \sum_i \frac{dX^i}{dB} \partial_{X^i} \tag{61}$$

and $K_\gamma(B) = \delta Q_{rev}(Z_B) = 1 - \sum_i \tilde{\xi}_i (dX^i/dB)$. For a curve $\gamma^0 : [0, B_0] \to \mathcal{D} \cup \{T = 0\}$ one has

$$S(\gamma^0(B_0)) = S(\gamma^0(0)) + \int_0^{B_0} dB \frac{K_{\gamma^0}(B)}{T(B, X^1(B), \dots, X^{n+1}(B))}. \tag{62}$$

One has to require that $K_{\gamma^0}(B)/T(B, X^1(B), \dots, X^{n+1}(B))$ is integrable near $B = 0$. We assume that $K_{\gamma^0}(B)$ is at least continuous, even at $B = 0$. The above integrability is then implemented. In fact, $1/T$ is integrable in $B = 0$ in order to obtain a finite entropy at $B = 0$ (for any B and any $X \equiv X^1, \dots, X^{n+1}$ it holds that $S(B, X) = S(0, X) + \int_0^B dY(1/T(Y, X))$, where the integral function is required to be continuous; see, e.g., appendix B of [1]). Note also that $K_{\gamma^0}(B) = 0$ corresponds to an isentropic path leaving $T = 0$. Moreover, for any $\gamma^0(B)$ such that (dX^i/dB) is finite as $B \to 0^+$ for all $i = 1, \dots, n+1$, one finds $K_{\gamma^0}(B) \to 1$ in that limit. There is no problem in allowing a non-vanishing $K_{\gamma^0}(B)$ in the limit as $B \to 0^+$.

Condition (Π) can be translated into

Condition ($\bar{\Pi}$). *For any simple curve $\gamma^0(B)$ starting at whichever point of the surface $B = 0$ and such that $K_{\gamma^0}(B)$ is continuous there exists a neighbourhood $(0, B_\epsilon(\gamma^0))$ where $K_{\gamma^0}(B) > 0$.*

This means that a system at $T = 0$ has to absorb heat in order to reach a state at $T > 0$. The double implication between ($\bar{\Pi}$) and (N) is very natural, and gives rise to the following result:

Result 7. *Let us assume the following: $S \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$; $\gamma^0 : [0, B_0] \to \mathcal{D} \cup \{T = 0\}$ is any simple oriented curve parametrized by B and such that its tangent vector Z_B is at least continuous in $[0, B_0]$. Then ($\bar{\Pi}$) is equivalent to (N).*

Proof. If (N) holds, one has that for any B, X it holds, with $S(0, X) = \Sigma_0$ because of (N) and $S(B, X) > \Sigma_0$ for any $B > 0$ due to strict monotonicity of S in B (in fact, $\partial S/\partial B = \partial S/\partial U = 1/T > 0$). Condition ($\bar{\Pi}$) is then easily deduced as in the previous section. Note that strict monotonicity of S in B has replaced the stability condition. The implication ($\bar{\Pi}$) $\Rightarrow$ (N) is obtained by showing that, if S is continuous at $T = 0$ and $T = 0$ is connected, a violation of (N) implies a violation of (Π). The proof consists in showing that a violation of (N) implies the existence of isentropic paths reaching $T = 0$, and it is the same as in section 5.6 of [1]. Again, strict monotonicity of S in B plays an important role. $\qquad\square$

7. Minimum entropy at $T = 0$

In the standard approach to Nernst's heat theorem in homogeneous thermodynamics, the entropy S goes to a finite minimum as $T \to 0^+$, as it can be easily deduced from the S–T diagrams. This minimum does not depend on the deformation parameters. It is also stated that the entropy of any given system attains the same finite least value for every state of least energy [24, 26].

We call $\min(S)$ *the following condition of minimum entropy at $T = 0$,*

$$S(T, X_1) \geqslant S(0, X_2) \qquad \forall T \geqslant 0, X_1, X_2 \tag{63}$$

where $X \equiv x^1, \ldots, x^{n+1}$. This condition amounts to a condition of absolute minimum for S at $T = 0$.

Result 8. *Let us assume that $\mathcal{D} \cup \{T = 0\} = I_T \times \mathcal{K}$ (cf. section 2), S belongs to $C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$ and it is a monotonically strictly increasing function of T. Then $\min(S) \Leftrightarrow (N)$.*

Proof. We first show that $\min(S) \Rightarrow (N)$. In fact, one has $S(0, X_2) \geqslant S(0, X_1)$, and also $S(0, X_1) \geqslant S(0, X_2)$. Thus, (N) holds. Strict monotonicity in T does not allow us to obtain states at $T > 0$ such that $S(T, X) = S_0 = S(0, Y)$. The converse implication $(N) \Rightarrow \min(S)$ follows trivially from $S(T, X) > S_0$ for all $T > 0$ and for all X; cf equation (39). $\qquad \square$

Note that if (N) is violated, S is continuous and $T^{-1}(0)$ is connected, then $S(0, X)$ depends on X in such a way that there exist points $(0, X_0)$ which are not local minima (see appendix D), against $\min(S)$. Note also that this condition does not require homogeneity.

One could obtain the above equivalence under the weaker condition

$\min_L(S)$: $S(T, X_1) \geqslant S(0, X_2)$ *for all $T \in [0, T_\epsilon)$ and for all X_1, X_2.*

This 'local' condition is called $\min_L(S)$ and implies (N) if a neighbourhood for any point $(0, X)$ exists, $S \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$ and strict monotonicity of S in T holds for $T \in (0, T_\epsilon^1)$ (even with $T_\epsilon^1 < T_\epsilon$). (N), the existence of a rectangular neighbourhood for any point $(0, X)$ and the aforementioned strict monotonicity in T imply $\min_L(S)$. Condition $\min_L(S)$ could also allow an absolute minimum at $T > 0$. Nevertheless, this weaker condition coincides with the above one in homogeneous thermodynamics. Moreover, on a connected thermodynamic domain, the requirement for the isentropic surfaces $S = $ const to be path-connected does not allow us to find a local minimum at $T = 0$ which is not a global minimum; in fact, it would belong to a surface $S = $ const but no isentropic path could reach it [1]. Note also that an absolute minimum of the entropy at $T > 0$ would be pathological in the same way as $S = 0$ at $T > 0$ is pathological in homogeneous thermodynamics, because heat can be only absorbed in a neighbourhood of this point by the system; see [1, 6].

A further weaker condition is

$\mathrm{locmin}(S)$: *each point of the surface $T = 0$ is a local minimum for S and $S(T, X) > S(0, X)$ for all $T \in (0, T_\epsilon)$ and for all X, X_0.*

(The latter condition is implemented if, e.g., $S \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$, $T^{-1}(0)$ is connected, a rectangular neighbourhood for any point $(0, X_0)$ exists and strict monotonicity in T holds for $T \in (0, T_\epsilon)$.) This weaker condition is called $\mathrm{locmin}(S)$. One has

Result 9. *Let us assume the following: S belongs to $C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$; $T^{-1}(0)$ is path-connected. Then $\mathrm{locmin}(S) \Rightarrow (N)$.*

Proof. The implication is a consequence of result 10 in appendix D. $\qquad \square$

We recall that, with reference to the surface $T = 0$, we use 'connected' and 'path-connected' interchangeably, in the sense that we assume that when $T = 0$ is connected it is also path-connected, and the same is true for each connected component.

The converse implication can be obtained easily: (N) the existence of a rectangular neighbourhood for any point $(0, X)$ and strict monotonicity of S in T for $T \in (0, T_\epsilon)$ imply $\mathrm{locmin}(S)$.

One can also work in regular coordinates B and $X \equiv X^1, \ldots, X^{n+1}$ introduced in section 2.2 and impose that $S(B, X_1) \geqslant S(0, X_2)$ for all $B \geqslant 0$, X_1, X_2. (N) again follows. One finds that strict monotonicity in B is ensured by $\partial S/\partial B = \partial S/\partial U = 1/T > 0$.

Note also that, if $C_X(T) < 0$ is allowed for $T \in (0, T_\epsilon)$, i.e., if S is monotonically strictly decreasing in T for $T \in (0, T_\epsilon)$, then min(S) can be replaced with max(S): $S(T, X_1) \leqslant S(0, X_2)$ for $T \in (0, T_\epsilon)$ and for all X_1, X_2. Moreover, if (N) holds when $C_X(T) < 0$ is allowed for $T \in (0, T_\epsilon)$, then the thermodynamic domain cannot be such that the coordinate B can be introduced (in fact, $S(B, X) > S(0, X) \equiv \Sigma_0$ for all X), and

$$S(U, X) = \Sigma_0 + \int_{U_0}^{U} dY \frac{1}{T(Y, X)} \tag{64}$$

where $T(U_0, X) = 0$, makes sense only for $U < U_0$. See also appendix C. In the case where B can be defined, the presence of C_{γ^0} negative near $T = 0$ means that (N) is violated. This happens, e.g., in the case of black holes [10].

8. The case of infinities in deformation parameters

If one relaxes the requirement of finite deformation parameters in the limit as $T \to 0^+$, then (N) can be easily violated, in the sense that the limit of S as $T \to 0^+$ can be made dependent on the deformation parameters and, e.g., violate Planck's restatement in standard homogeneous thermodynamics; see [5]. This violation of (N) can be obtained e.g., by requiring that the volume V is a divergent function $V(T)$ of T in the limit as $T \to 0^+$. The volume can, e.g., be allowed to diverge as a positive power of $1/T$ in that limit. In general, this kind of limit as $T \to 0^+$ can be taken along curves $\gamma(T)$ where at least one deformation parameter diverges. The result of the limit $\lim_{T \to 0^+} S$ depends on which kind of divergence of the deformation parameter as $T \to 0^+$ is assumed. In this sense, there is dependence of the limit on the diverging deformation parameter. In any case, (U) holds and it can be considered to be implemented as (U4) unattainability [2] (i.e., the state cannot be reached in any case, not only because it is not adiabatically linked with other states of the system), because infinities in deformation parameters appear to be actually non-implementable and, moreover, they are unphysical. As a consequence, we limit ourselves to considering an example in homogeneous thermodynamics.

We sketch an example concerning $S = VT^3$ ('Debye model'). Let us consider the curve γ in the (V, T)-plane $V(T) = a_0 T^{-3} + a_1 T^{-2}$, where $a_0 > 0$ and a_1 are constants. Then, for the Debye model, one finds $S \to a_0$ along γ. Any finite positive value for S in the limit as $T \to 0^+$ is allowed by changing a_0, and Planck's restatement is violated. Moreover, $C_\gamma(T) = a_1 T$. If $a_1 < 0$, then $C_\gamma(T) < 0$ in a right neighbourhood of $T = 0$. Isentropic paths approaching $T = 0$ are allowed (for $a_1 = 0$) but they cannot be performed for reaching $T = 0$ and (U4) holds. Moreover, for $V(T) = a_2 T^{-4}$ one finds that S diverges as $T \to 0^+$.

As clearly stated by Landsberg [2], a decoupling between the validity of (U4) and the validity of (N) occurs, as also appears from the present analysis. Moreover, if infinities in the deformation parameters are allowed, then any value of S and any divergent behaviour can be allowed. A further note is that the thermodynamic limit of statistical mechanics does not imply an 'interference' between the limit as $V, N \to +\infty$ and the limit as $T \to 0^+$ in such a way that (N) can be jeopardized as above; in fact, the limit as $T \to 0^+$ has to be taken after the thermodynamic limit is implemented, as remarked by Griffiths [27]. One has first to ensure that a thermodynamic system is at hand, which is obtained by taking the thermodynamic limit; only then can one consider the limit as $T \to 0^+$. See also [1] and references therein.

9. Notes on phase coexistence and on mixtures

This case is more difficult, we limit ourselves to the case of standard thermodynamics, for which a set-up of a general framework should require a further analysis. Let us first assume that, for a two-phase one-component system, the coexistence domain of two phases I and II can arbitrarily approach the absolute zero of temperature. The latent heat associated with the phase transition is $Q_{I \to II} = \Delta H_{II}^{I} = T_{transition} \Delta S_{II}^{I}$. It has to vanish as $T \to 0^+$ (see e.g. [28]). As far as the entropy is concerned, in the presence of a first-order phase transition, there is a discontinuity in the molar entropy of the two phases. Moreover, the third law for each phase implies that

$$\lim_{T \to 0^+} \Delta S_{II}^{I} = 0. \tag{65}$$

The latter result is usually stated as the vanishing of entropy differences along any isothermal reversible process. It is well known that, at the phase coexistence, the Clapeyron–Clausius equation holds,

$$\Delta S_{II}^{I} = -\Delta V_{II}^{I} \left(\frac{dp}{dT} \right)_{coex}. \tag{66}$$

From (65) it follows that

$$\lim_{T \to 0^+} \left(\frac{dp}{dT} \right)_{coex} = 0. \tag{67}$$

Equation (67) can also be seen as a consequence of a continuity boundary condition for thermodynamics at $T = 0$ introduced in [1]. An apparent exception to the vanishing of the latent heat as $T \to 0^+$ seems to be represented by sublimation latent heat of several substances [29]. Actually, even if the molar latent heat does not vanish in the limit as $T \to 0^+$, the third law is preserved, because the number of particles in the gas phase vanishes very rapidly in the limit as $T \to 0^+$, thus the corresponding entropy vanishes and, *a fortiori*, $T \Delta S$ vanishes and no sublimation occurs at absolute zero [29].

A more complex situation appears if one allows for two thermodynamic degrees of freedom [20] at the phase coexistence. This can happen, e.g., when for a two-component mixture two phases are allowed. In fact, according to Gibbs' phase rule, the coexistence region is a two-dimensional submanifold ($f = 2$ [20]). In this case, by choosing (p, T) as independent variables, one finds that the molar fraction $X \in [0, 1]$ of the second component becomes a function of (p, T) instead of being a third independent variable as in the presence of a single phase ($f = 3$). In the following, $X^{(1)}$, $X^{(2)}$ indicates the molar fraction of the second component in phases (1) and (2) respectively. An analogous notation is used for indicating the phase one is referring to. Note also that $X = X^{(1)} + X^{(2)}$. From the van der Waals equation [30], one obtains

$$\frac{\partial X^{(1)}}{\partial T} = -\frac{S^{21}}{X^{(2)} - X^{(1)}} \frac{1}{(\partial^2 G^{(1)}/\partial(X^{(1)})^2)} \tag{68}$$

$$\frac{\partial X^{(2)}}{\partial T} = -\frac{S^{12}}{X^{(1)} - X^{(2)}} \frac{1}{(\partial^2 G^{(2)}/\partial(X^{(2)})^2)} \tag{69}$$

$$\frac{\partial X^{(1)}}{\partial p} = +\frac{V^{21}}{X^{(2)} - X^{(1)}} \frac{1}{(\partial^2 G^{(1)}/\partial(X^{(1)})^2)} \tag{70}$$

$$\frac{\partial X^{(2)}}{\partial p} = +\frac{V^{12}}{X^{(1)} - X^{(2)}} \frac{1}{(\partial^2 G^{(2)}/\partial(X^{(2)})^2)} \tag{71}$$

where the following expressions

$$S^{21} \equiv (S^{(2)} - S^{(1)}) - (X^{(2)} - X^{(1)})\frac{\partial S^{(1)}}{\partial X^{(1)}} \tag{72}$$

$$V^{21} \equiv (V^{(2)} - V^{(1)}) - (X^{(2)} - X^{(1)})\frac{\partial V^{(1)}}{\partial X^{(1)}} \tag{73}$$

and those obtained by substituting $(1) \mapsto (2)$, $(2) \mapsto (1)$ appear. The third law $S \to 0^+$ *and* differential criteria (under the hypotheses of section 4) imply that $(\partial X^{(1)}/\partial T) \to 0$ and $(\partial X^{(2)}/\partial T) \to 0$ as $T \to 0^+$. Non-critical mixing is required.

The problem for (N) in the presence of mixtures arises when ideal mixtures are taken into account. In fact, in an ideal mixture the so-called mixture entropy, depending only on the molar fractions, arises. If the ideal mixture can be considered to be ideal even in the limit $T \to 0^+$, then a violation of (N) occurs [31]. In order to avoid this violation, it is necessary to postulate that either the mixture becomes non-ideal near $T = 0$ or it separates into its components [26]. Diluted binary mixtures ^{3}He–^{4}He are non-ideal and $S \to 0^+$ is respected in statistical mechanical calculations [32].

10. Conclusions

We have discussed further conditions which ensure the validity of the third law in its entropic form. We have introduced the framework in which $T = 0$ appears as an independent thermodynamic coordinate and also a heuristic picture for non-homogeneous thermodynamics generalizing the standard one. Properties of S and of the thermodynamic domain have been analysed. Then, we have recalled some differential criteria ensuring (N), by pointing out that they correspond to sufficient but not necessary conditions for (N). Then, a new condition ensuring the validity of (N) has been introduced and discussed. In particular, condition (Π) has been shown to be the condition involving the vanishing of heat capacities as $T \to 0^+$ which is able to ensure (N). Its physical meaning is very clear, and amounts to the impossibility of leaving the surface $T = 0$ without heat absorption by the system. It is a physical condition which does not refer to any statistical mechanical framework, to the problem of the Carnot–Nernst cycle (see the discussion in [1]), or to the problem of the adiabatic inaccessibility (even if, by construction, it implies adiabatic inaccessibility of the surface $T = 0$). Also a heuristic justification has been given. Then, a translation of condition (Π) adapted to the Gibbsian framework, the condition of minimum entropy at $T = 0$ and their equivalence with (N) have been discussed. The failure of (N) occurring if infinite deformation parameters are allowed and a look at the problem of phase coexistence and mixtures have also been briefly addressed.

In [7] we have introduced a generalized framework for thermodynamics where the homogeneity symmetry is substituted with quasi-homogeneity symmetry. Some considerations about (N) in quasi-homogeneous thermodynamics are in order. Also in the quasi-homogeneous case, (N) holds if and only if $\lim_{T \to 0^+} S = 0$. Note that the absence of concavity and of thermal stability can occur, but this does not necessarily mean that (N) is violated; cf also [10]. If (N) holds, then S gets its absolute minimum $S = 0$ at $T = 0$, and, if one does not allow points having $S = 0$ at $T > 0$, (Π) is also implied. The equivalence between $(\bar{\Pi})$ and (N) runs as in section 6.

Acknowledgments

Appendix A. Equivalence of various conditions ensuring (N)

We have shown that both condition (Π) and condition (HOM) discussed in [1] are equivalent to (N) for homogeneous systems. As a consequence, they are equivalent conditions: (HOM) $\Leftrightarrow$ (Π). The same is true if condition ($\bar{\Pi}$) is taken into account.

We recall that, in standard homogeneous thermodynamics, many assumptions are automatically implemented. Any point of the boundary $T = 0$ of the domain epi(b) has a rectangular neighbourhood. Moreover, the domain is star-shaped with respect to any point. Concavity of S, which, together with homogeneity, in the Gibbsian framework ensures that S is superadditive [9], ensures also that thermal stability property (a) holds. These properties allow a very natural equivalence between various conditions leading to (N). The non-homogeneous case requires instead more *ad hoc* hypotheses. See below.

As far as $\min(S)$ is concerned, it is evident that it is equivalent to (N) in the homogeneous case. In standard homogeneous thermodynamics for S as a function of $T, x^1, \ldots, x^{n+1}$ the following property holds: if S is continuous in the limit as $T \to 0^+$, then (N) holds if and only if $T = 0$ is a leaf of the thermodynamic foliation [1].

A.1. Non-homogeneous case

If one relaxes homogeneity and convexity, one can still find a relation between (N), (Π) and $\min(S)$. By referring to the hypotheses
$S \in C^1(\mathcal{D})$ *(default hypothesis)* and

 (a) *S is a monotonically strictly increasing function of T at least for $T \in (0, T_\epsilon)$,*
 (b) $S \in C^1(\mathcal{D}) \cap C(\mathcal{D} \cup \{T = 0\})$,
 (c) *any point $(0, X)$ has a rectangular neighbourhood,*
 (d) $T^{-1}(0)$ *is connected,*

one can infer from the previous sections that

$\{(a), (c), (N)\} \Rightarrow (\Pi)$;

$\{(a), (b), (c), (d), (\Pi)\} \Rightarrow (N)$ or also $\{(c), (d), (22), (23), (\Pi)\} \Rightarrow (N)$;

$\{(a), (b), (c), \min_L(S)\} \Rightarrow (N)$;

$\{(a), (c), (N)\} \Rightarrow \min_L(S)$.

Moreover,

$\{(b), (d), \text{locmin}(S)\} \Rightarrow (N)$;

$\{(a), (c), (N)\} \Rightarrow \text{locmin}(S)$;

$(N) \Rightarrow (\bar{\Pi})$,

$\{(b), (d), (\bar{\Pi})\} \Rightarrow (N)$.

As far as the 'leaf' property of the (connected) surface $T = 0$ is concerned, we refer to the Gibbs-like framework where coordinates B and $X \equiv X^1, \ldots, X^{n+1}$ are allowed. We assume the hypothesis (b) of continuity for S. One can show that, if (N) is violated, there are isentropic

paths reaching $T = 0$ in exactly the same way as in section 5.6 of [1]. If $T = 0$ has to be a leaf, (N) has to hold. Moreover, it is also true that, if (N) holds in the aforementioned framework, then $T = 0$ is a leaf. In fact, $S(B, X) > \Sigma_0$ for any $B > 0$ whichever value of X is considered. This means that the surface $S = \Sigma_0$, which is the only one allowed to intersect $T = 0$, actually coincides with $T = 0$. Then, $T = 0$ is a leaf.

We recall that the 'leaf' property is important, without it adiabatic inaccessibility is jeopardized and one does not obtain a foliation of the whole thermodynamic domain into disconnected adiabatic surfaces [1]. In this sense, (N) corresponds to a regularity condition of the Pfaffian equation $\delta Q_{\text{rev}} = 0$ at the surface $T = 0$, as in the homogeneous case [1].

By following section 5.6 of [1], one shows that, if in Gibbs-like coordinates $\delta Q_{\text{rev}} \in C^1(\mathcal{D} \cup \{T = 0\})$, then $T = 0$ is a leaf of the thermodynamic foliation. In fact, any Cauchy problem for integral curves of $\delta Q_{\text{rev}} = 0$ with initial point on the surface $T = 0$ has one solution entirely within the $T = 0$ surface by hypothesis, and, being Lipschitz property satisfied, such a solution is unique. See section 5.6 for details (note that section 5.6 of [1] holds true in the general case, apart from section 5.6.3).

If the boundary is described by $y^0 = 0$ in local coordinates $y^0, \ldots, y^{n+1}$ as in section 5.5.1 of [1], then $\delta Q_{\text{rev}} = \sum_{i=0}^{n+1} a_i(y^0, \ldots, y^{n+1}) \, dy^i$ and $T = 0 \Leftrightarrow y^0 = 0$; moreover $y^0 = 0$ is a codimension 1 integral manifold iff $a_i(y^0 = 0, y^1, \ldots, y^{n+1}) = 0$ for all $i > 0$, and $a_0(y^0 = 0, y^1, \ldots, y^{n+1}) > 0$ is assumed ($a_0(y^0 = 0, y^1, \ldots, y^{n+1}) \neq 0$ because δQ_{rev} is non-singular [1]). As a consequence, $\partial S/\partial y^0 = a_0/T > 0$ in a right neighbourhood of $y^0 = 0$ by continuity. This means that in such a neighbourhood S is monotonically increasing in y^0. In the following, let us put $y \equiv y^1, \ldots, y^{n+1}$.

The double implication $(\bar{\Pi}) \Leftrightarrow (N)$ is still true because a local monotonicity in y^0 is allowed. One has to consider y^0 as a curve parameter in place of B and obvious changes in the proof.

Also the double implication of (N) with the requirement that each point belonging to the surface $y^0 = 0$ is a local minimum for S (cf locmin(S)) holds true because of this local monotonicity in y^0. If each point $(0, \bar{y})$ is a local minimum for a continuous S and $T = 0$ is connected, then (N) holds (cf results 9 and 10), and there exists a neighbourhood V of $(0, \bar{y})$ such that $S(y^0, y) \geqslant S(0, \bar{y})$ in V; moreover, by continuity, there exists a neighbourhood W of $(0, \bar{y})$ such that $a_0(y^0, y) > 0$ in W. Then, one finds that $S(y^0, y) > S(0, \bar{y})$ for $y^0 > 0$ in a neighbourhood $V \cap W$ of $(0, \bar{y})$.

If (N) holds and $T = 0$ is connected, then each $(0, \bar{y})$ is a local minimum because of the aforementioned local monotonicity of S as a function of y^0. In fact, it holds $S(y^0, y) \geqslant S(0, y) \equiv S_0$ for each $(y^0, y) \in W$ and $S(y^0, y) = S_0$ only if $y^0 = 0$.

Appendix B. Failure of thermal stability and non-equivalence of (U) and (N)

We preliminarily note that this appendix can be better understood after a reading of section 5.1. We give some simple examples where (N) and (U) are shown to be inequivalent if thermal stability is suitably violated. The essential point is that, by allowing the heat capacities $C_{x^1,\ldots,x^{n+1}}(T)$ to have both positive and negative values near $T = 0$, one can easily obtain that (N) holds and the conventional (U), intended as the absence of isentropes reaching $T = 0$, necessarily fails. Let us, e.g., consider the toy-model entropy introduced at the end of section 5.1.2, $S(T, x) : [0, T_1) \times (x_0, x_2) \to \mathbb{R}$, defined by $S(T, x) = T(x_1 - x) + \Sigma_0$, with $x_2 > x_1 > x_0$ and $\Sigma_0 \geqslant T_1(x_2 - x_1)$ a non-negative constant; this function can be continued also in the region $T > T_1, x > x_2$ by means of another function. S satisfies (N) and the line $x = x_1$ allows $T = 0$ to be reached isentropically. Thus, conventional (U) is violated. If a form of unattainability still holds, then one has to suppose that some hindrance

in performing the above line occurs; Landsberg hypothesizes the existence near $T = 0$ of an abrupt discontinuity in order to justify such a hindrance [2]; cf also [1, 10].

It is still possible to obtain the standard implication $(N) \Rightarrow (U)$ if, e.g., $T^{-1}(0)$ is *not* connected, say, $T^{-1}(0) = A \cup B$, with A and B open sets such that $A \cap B = \emptyset$. Then, if one requires that near $T = 0$ the heat capacity C_x is positive in the branch A and negative in the branch B, and moreover, (N) holds, then (U) holds in the conventional sense. Let us again consider the above entropy $S(T, x) = T(x_1 - x) + \Sigma_0$, where this time the domain is $([0, T_1) \times (x_0, x_1 - \epsilon)) \cup ([T_0, T_1) \times [x_1 - \epsilon, x_1 + \epsilon]) \cup ([0, T_1) \times (x_1 + \epsilon, x_2))$, where $\epsilon > 0$ is a small constant. There is a branching this time, the interval $[x_1 - \epsilon, x_1 + \epsilon]$ does not belong to $T = 0$, (N) holds, C_x is positive near $T = 0$ for $x \in (x_0, x_1 - \epsilon)$ and negative for $x \in (x_1 + \epsilon, x_2)$. In this domain, the isentrope $x = x_1$ is not allowed to reach $T = 0$, and unattainability in the conventional sense is implied. Of course, this multi-branching is *ad hoc*, nevertheless it is a valid example of what should occur in order to allow a conventional implication $(N) \Rightarrow (U)$.

The converse implication, where (U) is intended again in the conventional sense, in the presence of heat capacities of both signs is instead impossible in general, because even if the following two necessary conditions occur,

- a multi-branching occurs, say, into two branches,
- condition (Π) holds in a branch and the opposite condition $C_{\gamma_0}(T) < 0$ holds in a neighbourhood of $T = 0$ in the other branch,

one has still to require that the limit of S as $T \to 0^+$ is the same on the two branches. As far as the latter condition is also to be imposed by hand and it amounts to (N), there is no way to obtain (N) from (U) under the above hypothesis of non-definite signs for heat capacities near $T = 0$.

See also [10], where this topic concerning the inequivalence of (U) and (N) is also dealt with.

Appendix C. Branch $T \to 0^+$ as $U \to +\infty$

In general, when the heat capacity is negative definite, the limit $T \to 0^+$ can be obtained both for finite values of U and for $U \to +\infty$. In the former case, U has a finite upper bound, $U \leqslant U_0 < +\infty$, because $T \geqslant 0$ decreases for increasing U (and vice versa) and, by defining $X \equiv X^1, \ldots, X^{n+1}$, it holds that

$$T(U, X) = T(U_0, X) + \int_{U_0}^{U} dU \frac{1}{C_X(U)}. \tag{C.1}$$

If $T(U_0, X) = 0$, then $T \geqslant 0$ only for $U \leqslant U_0$. Let us, e.g., consider the toy model $S(U, V) = S_0 - 2\sqrt{U_0 - U} V$, with $U_1 \leqslant U \leqslant U_0$, $V_1 \leqslant V \leqslant V_0$, and S_0 is a constant such that $S_0 \geqslant \max_{U,V}(2\sqrt{U_0 - U} V)$. One finds $T = \sqrt{U_0 - U}/V$, $U = U_0 - V^2 T^2$ and that the heat capacity is negative. Moreover, $T \to 0^+$ holds iff $U \to U_0^-$. In this model, (N) holds.

Maybe $T = 0$ can also be approached only for $U \to +\infty$, as the toy model $S = U^2/V$ shows. One finds $T = V/(2U)$, i.e., $U = V/(2T)$ and $S = V/(4T^2)$. In the case where $T \to 0^+$ as $U \to +\infty$ is implemented and $S \to +\infty$ in this limit, it is also possible to check if (N) holds; one has to check if

$$\lim_{T \to 0^+} [S(T, x^1, \ldots, x^{n+1}) - S(T, \bar{x}^1, \ldots, \bar{x}^{n+1})] = 0 \tag{C.2}$$

holds or fails (note that the aforementioned check in the case of the classical ideal gas is analogous). In the above model one finds a violation of (N), in fact for $V \neq \bar{V}$

one finds $\lim_{T \to 0^+}(S(T, V) - S(T, \bar{V})) \neq 0$. Note also that $\lim_{T \to 0^+} S(T, x^1, \ldots, x^{n+1})/S(T, \bar{x}^1, \ldots, \bar{x}^{n+1}) = 1$ is *not* a sufficient condition for (N) in the case of diverging entropy, because of the possible presence of sub-leading terms which still do not allow that $(C.2)$ holds; cf [10] for the black hole case. Even in the case where (N) fails, unattainability is automatically ensured as $(U4)$ unattainability, because $U = +\infty$ is trivially a forbidden value.

There is also an even more exotic possibility, which is interesting because black hole thermodynamics implements it. Let us consider a somehow special case in which the heat capacity $C_{x^1, \ldots, x^{n+1}}(T)$ is allowed to change sign. For definiteness, let us assume that $\lim_{T \to T_0} C_{x^1, \ldots, x^{n+1}}(T) = 0$, $C_{x^1, \ldots, x^{n+1}}(T) > 0$ for $0 < T < T_0$ and $C_{x^1, \ldots, x^{n+1}}(T) < 0$ for $T_0 < T$. Being $\partial U/\partial T = C_{x^1, \ldots, x^{n+1}}$, this means that U is an increasing function of T for $0 < T < T_0$ and a decreasing function of T for $T_0 < T$. By inverting, one finds that, on the negative heat capacity branch, T decreases as U increases and one can obtain a vanishing T in the limit $U \to +\infty$. This happens, e.g., in the thermally unstable branch of black hole thermodynamics, where $T \to 0^+$ can be obtained by sending the mass M of the black hole to infinity at fixed other black hole parameters; see [10]. In this case, one can obtain $S \to +\infty$ in the limit as $T \to 0^+$ at fixed $x^1, \ldots, x^{n+1}$, as the black hole case shows. We do not explore this topic further, referring to [10] for further details concerning the black hole case.

Appendix D. Violation of (N) and presence of points which are not local minima for S

Result 10. *If $S \in C(\mathcal{D} \cup \{T = 0\})$ and $T^{-1}(0)$ is pathwise connected, then a violation of (N) implies the existence of points belonging to the surface $T = 0$ which are not local minima for S.*

Proof. If $(0, x_0^1, \ldots, x_0^{n+1})$ is a local minimum for S, then it is also a local minimum for Σ. Let us define $X \equiv x^1, \ldots, x^{n+1}$ and consider a continuous function $f(X)$ such that each point of the boundary ∂A of its domain A is a local minimum. Let ∂A be path-connected. Given two boundary points Y and Z, let us consider a continuous simple path $\gamma_{YZ}(t) : [0, 1] \to \partial A$ such that $\gamma_{YZ}(0) = Y$ and $\gamma_{YZ}(1) = Z$. Then let us consider $F(t) \equiv f(\gamma_{YZ}(t))$, which is a continuous function. The Weierstrass theorem ensures that F gets an absolute maximum in $[0, 1]$. This absolute maximum $t_{\max}$ corresponds to a point X_m. The requirement for X_m to be also a local minimum imposes that F is constant along the aforementioned path. In fact, there exists a neighbourhood $t_1 < t_m < t_2 \subset [0, 1]$ such that $F(t_m) \leqslant F(t)$ because X_m is a local minimum; the inequality $F(t_m) \geqslant F(t)$ for all $t \in [0, 1]$ implies that $F(t) = F_m = $ const in (t_1, t_2). Moreover, one has that, for small $\epsilon > 0$, $F(t_1 + \epsilon) = F_m$ and $\lim_{\epsilon \to 0^+} F(t_1 + \epsilon) = \lim_{t \to t_1} F(t) = F_m$, where the latter equality is due to continuity. Then t_1 corresponds both to a local minimum and to an absolute maximum. Then, there exists a $0 \leqslant t_3 < t_1$ such that F is constant. By iterating, one finds that F has to be constant on the whole interval $[0, 1]$. The path chosen being generic, it follows that F has to be constant on ∂A. As a consequence, Σ has to be constant at the surface $T = 0$ if all the points belonging to $T = 0$ are local minima. $\square$

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