# Homogeneity as a bridge between Carathéodory and Gibbs

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(November 2, 2018)

In this paper we show that the homogeneity of the Pfaffian form representing the infinitesimal heat exchanged reversibly  $\delta Q_{rev}$  by a thermodynamic system allows to find immediately and explicitly an integrating factor. An interesting bridge between Carathéodory's approach to thermodynamics and Gibbs' approach is established.

PACS: 05.70.-a

## I. INTRODUCTION

One can distinguish in general between two main formal approaches to thermodynamics. On one side there is the approach due to Carathéodory, which is based on the integrability of the Pfaffian form  $\delta Q_{rev}$  [1–12] and represents the development of the line of thought which starts with Clausius and Kelvin. On the other side one finds the approach due to Gibbs, in which S is postulated to be an extensive concave function of the extensive variables [13–15]; further developments of this approach, from the point of view of its axiomatization, find their latest realization in Ref. [16]. Our aim in this paper is not to propose an axiomatics for thermodynamics from first principles, but simply to discuss a formalism which represents a straightforward link between Carathéodory's approach and Gibbs' approach to thermodynamics and to propose a set of constructive assumptions which lead to standard thermodynamics. We know that Carathéodory's postulate of adiabatic inaccessibility ensures the integrability of the Pfaffian form  $\delta Q_{rev}$  [3–7,9,10]; in particular the so-called metrical entropy S and the so-called absolute temperature T exist and

 $\delta Q_{rev} = T \ dS.$ 

We choose to work in the framework of Carathéodory's approach, thus we assume the integrability of the Pfaffian form  $\delta Q_{rev}$ . Moreover, we apply this formalism to (maybe multi-component) homogeneous simple systems, and choose the extensive variables  $(U, V, X^1, \ldots, X^n)$  as independent coordinates in the equilibrium thermodynamics space [for "extensive" we mean "positively homogeneous functions of degree one"]. Notice that these variables characterize Gibbs' approach in the entropy representation, they characterize the so-called Gibbs space [15]; moreover they can be considered as the natural variables to be concerned with in the framework of an approach where the entropy and the temperature have not yet been introduced. In the following, the main assumptions of our construction are indicated as h1),h2),h3),h4),h5),h6),h7),h8),h9),h10) in the text. We start from h1):

h1) In our approach the homogeneity of the system is translated into the homogeneity of degree one of the integrable Pfaffian form

$$\delta Q_{rev} = dU + p \, dV - \sum_{i} \xi_i \, dX^i. \tag{1}$$

This means that, under the rescaling  $(U, V, X^1, \ldots, X^n) \mapsto (\lambda U, \lambda V, \lambda X^1, \ldots, \lambda X^n)$  one find  $\delta Q_{rev} \mapsto \lambda \, \delta Q_{rev}$ . See the following section for more details.  $p, \xi_1, \ldots, \xi_n$  are intensive variables.

From a physical point of view, the homogeneity of  $\delta Q_{rev}$  can be phenomenologically inferred by the observation of the extensivity of  $U, V, X^1, \ldots, X^n$  and the intensivity of  $p, \xi_1, \ldots, \xi_n$  in the case of standard thermodynamic systems. Our main point is the following. Because of a symmetry of the Pfaffian form for homogeneous systems, we are able to find an explicit integrating factor for  $\delta Q_{rev}$  and to construct a potential which is identified with the entropy, in particular, with the entropic fundamental equation of Gibbs. In particular, both the entropy and the temperature appear as derived quantities. More general constructions for thermodynamics under the hypothesis of a non-trivial symmetry for  $\delta Q_{rev}$  are studied in [17,18].

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### **II. HOMOGENEOUS PFAFFIAN FORMS**

In the following, we assume that the differential 1-form  $\omega$  is at least  $C^1$  in the domain  $\mathcal{D}$ . We define  $\Omega^k(\mathcal{D})$  as the set of all the k-forms (with a suitable degree of smoothness) defined on  $\mathcal{D}$ . We give below some relevant definitions. By "symmetry" for a differential 1-form  $\omega$  we mean that, if Z is a vector field and  $L_Z : \Omega^1(\mathcal{D}) \to \Omega^1(\mathcal{D})$  is the Lie derivative along it, we have

$$L_Z \ \omega \wedge \omega = 0. \tag{2}$$

The interested reader is referred to Ref. [19] and in particular also to Ref. [20], where the notions of homogeneous integrable Pfaffian forms and symmetry are found, and the corresponding integrating factor is deduced. The definition of homogeneous 1-form we give below is the same as the one appearing in [21]. An homogeneous 1-form of degree k + 1

$$\omega(x^1,\ldots,x^n) \equiv \sum_{i=1}^n \omega_i(x^1,\ldots,x^n) \, dx^i,\tag{3}$$

is, by definition, such that the coefficients  $\omega_i(x^1,\ldots,x^n)$  are homogeneous functions of degree k:

$$\omega_i(\lambda \ x^1, \dots, \lambda \ x^n) = \lambda^k \ \omega_i(x^1, \dots, x^n) \ \forall \ i = 1 \dots n.$$
(4)

In the case of an homogeneous 1-form the so-called radial vector field (which could be called also "Liouville field" [21])

$$Y \equiv \sum_{i=1}^{n} x^{i} \frac{\partial}{\partial x^{i}}$$

$$\tag{5}$$

is a symmetry for  $\omega$ . In fact, if x stays for  $x^1, \ldots, x^n$ , one has that the flow of the vector field Y is  $\phi_t(x) = x \exp(t)$ , thus

$$L_Y \ \omega = (k+1) \ \omega. \tag{6}$$

If the form is integrable and  $\omega(Y) \neq 0$ , then  $\omega(Y)$  is an integrating factor for  $\omega$ . This follows from the integrability condition

$$\omega \wedge d\omega = 0 \tag{7}$$

and from the definition of "symmetry". The condition  $\omega(X) \neq 0$  for a generic symmetry generator X is equivalent to the requirement that the symmetry is nontrivial according to the definition of Ref. [19], i.e., the vector field X does not belong to the distribution P of codimension one associated with the kernel of  $\omega$ . This means that the symmetry "shuffles" the leaves of the foliation associated with the integrable Pfaffian form  $\omega$  but it leaves the foliation itself invariant (instead a trivial symmetry preserves each leaf) [19]. From a geometrical point of view, a trivial symmetry is tangent to the foliation, a nontrivial one is transverse to the foliation. Note that in Ref. [20] a homogeneous Pfaffian form such that  $\omega(Y) \neq 0$  is called *non-dicritical*. We sketch here the proof that  $\omega(Y)$  is an integrating factor for the sake of completeness; an equivalent but more elementary proof, based on a "by hand" verification, is found in Appendix A. f is an integrating factor for  $\omega$  if

$$d\left(\frac{\omega}{f}\right) = 0,$$

that is

$$f \, d\omega - df \wedge \omega = 0.$$

We verify that  $\omega(Y)$  satisfies the latter equation:

$$\omega(Y)d\omega - (d\omega(Y)) \wedge \omega =$$
  
( $i_Y(\omega)$ ) $d\omega - ((di_Y)(\omega)) \wedge \omega =$   
( $i_Y(\omega)$ ) $d\omega - (L_Y\omega) \wedge \omega + (i_Y(d\omega)) \wedge \omega =$   
 $i_Y(\omega \wedge d\omega) = 0$ 

where we have introduced the standard contraction operator  $i_Y : \Omega^1(\mathcal{D}) \to \Omega^0(\mathcal{D})$  and we have used (2),(7) and also standard identities  $(d\omega(Y) = (di_Y)(\omega) = (L_Y - i_Y d)(\omega) = L_Y \omega - i_Y (d\omega)$  and  $i_Y(\omega \wedge d\omega) = (i_Y(\omega))d\omega + ((i_Y d)(\omega)) \wedge \omega$ .

### **III. THERMODYNAMIC ENTROPY REVISITED**

In the framework of thermodynamics of homogeneous systems, the domain  $\mathcal{D}$  of  $\delta Q_{rev}$  is assumed to be an open convex set (in the discussion of the third law the boundary T = 0 is introduced). Convexity of  $\mathcal{D}$  is related to the request of a concave entropy (see the following subsections). From a mathematical point of view, homogeneity forces the domain  $\mathcal{D}$  to be closed under multiplication by a positive real scalar  $\lambda$ , i.e. for each  $(U, V, X^1, \ldots, X^n) \in \mathcal{D}$  it has to hold  $(\lambda U, \lambda V, \lambda X^1, \ldots, \lambda X^n) \in \mathcal{D}$ . This means that  $\mathcal{D}$  has to be a cone, thus it has to be a convex cone. Given a convex set  $\mathcal{C}$ , a convex cone can be easily constructed, in fact the set

 $\mathcal{K}_{c} = \{ (\lambda U, \lambda V, \lambda X^{1}, \dots, \lambda X^{n}) | (U, V, X^{1}, \dots, X^{n}) \in \mathcal{C}, \lambda > 0 \}$ 

is the smallest convex cone containing C and it has the property to be closed under addition (see [22], pp. 13-14). Notice that D is also a  $C^{\infty}$  differentiable manifold.

The Pfaffian form  $\delta Q_{rev}$  is assumed to be of class at least  $C^1(\mathcal{D})$ , which is a rather general condition for the validity of Frobenius' theorem. [According to Ref. [16], a more general setting should be allowed, where the intensive variables are only locally Lipschitz-continuous. This requirement, which is physically well-grounded [16], would require a more general setting for Frobenius' theorem. In fact, the Pfaffian form  $\delta Q_{rev}$  would be locally Lipschitz-continuous, which implies that  $d(\delta Q_{rev})$  exists only almost everywhere, thus also the integrability condition is defined only a.e. We don't deal with this problem herein]. Then the intensive variables  $p(U, V, X^1, \ldots, X^n)$  and  $\xi_i(U, V, X^1, \ldots, X^n)$ , for  $i = 1, \ldots, n$ , belong to  $C^1(\mathcal{D})$  (at least); they are supposed to be known functions of the extensive variables. The Liouville operator is

$$Y = U \frac{\partial}{\partial U} + V \frac{\partial}{\partial V} + \sum_{i} X^{i} \frac{\partial}{\partial X^{i}}.$$
(8)

### **h2**) We require that the homogeneity symmetry of $\delta Q_{rev}$ is nontrivial.

Then, an integrating factor for  $\delta Q_{rev}$  can be immediately deduced from the homogeneity property, and it is given by

$$f(U, V, X^1, \dots, X^n) \equiv i_Y(\omega) = U + p V - \sum_i \xi_i X^i \neq 0.$$
 (9)

As a consequence,

$$\frac{\delta Q_{rev}}{f} \tag{10}$$

is a closed and, moreover, exact 1-form (being the domain simply connected). Thus

$$\frac{dU + p \, dV - \sum_i \, \xi_i \, dX^i}{U + p \, V - \sum_i \, \xi_i \, X^i} \equiv d\hat{S} \tag{11}$$

where  $\hat{S}$  is a potential for the form. The 1-form  $d\hat{S}$  is an homogeneous function of degree zero, as it follows from (11); in fact, the integrating factor f is an homogeneous function of degree one:

$$Y f = Y i_Y(\omega) = i_Y L_Y \omega = i_Y \omega = f$$

(the Cartan formula  $L_X i_Y - L_Y i_X = i_{[X,Y]}$  holds), and the infinitesimal heat exchanged reversibly is an homogeneous function of degree one. The exact Pfaffian form in (11) has coefficients  $(1/f, p/f, -\xi_1/f, \ldots, -\xi_n/f)$  which are homogeneous functions of degree -1. Then  $\hat{S}$  can be found only by quadratures (cf. [23], p. 16-20). One has

$$\hat{S}(U, V, X^{1}, \dots, X^{n}) - \hat{S}(U_{0}, V_{0}, X^{1}_{0}, \dots, X^{n}_{0}) = \int_{\Gamma} \frac{dU + p \, dV - \sum_{i} \xi_{i} \, dX^{i}}{U + p \, V - \sum_{i} \xi_{i} \, X^{i}}$$
(12)

where  $(U_0, V_0, X_0^1, \ldots, X_0^n)$  is a reference state and  $\Gamma$  is any reversible path connecting the reference state to the state  $(U, V, X^1, \ldots, X^n)$  of interest [a path is a oriented curve in the thermodynamic domain which is at least piecewise  $C^1$ ; one could also require, without loss of generality that the path is also simple, that is, non self-intersecting. A path, being defined along equilibrium states of the thermodynamic manifold, is, as a consequence, reversible in the sense of Refs. [7,14]].

h3) We require that the thermodynamic foliation is defined by the leaves  $\hat{S} = \text{const.}$  everywhere in  $\mathcal{D}$ .

As a consequence,  $\hat{S}$  is required to be a well-defined function for each state belonging to the thermodynamic domain  $\mathcal{D}$ . This assumption is natural in our framework; its necessity emerges in light of the discussion of the following subsections, in particular of subsections III C and III D.

# h4) We require that the integrating factor f is non-negative

The non-triviality condition  $f \neq 0$  is enforced by requiring that f is of definite sign [one could also ask for  $f \leq 0$ , the choice f > 0 is made on a conventional basis]. The relation of hypothesis h4) with thermodynamics is evident from the following subsection, being related to the non-negative definiteness of the absolute temperature.

# A. extensive entropy

The potential  $\hat{S}$  is related to the logarithm of a positive definite extensive potential H

$$\hat{S} - \hat{S}_0 = \log\left(\frac{H}{H_0}\right),\tag{13}$$

where Y H = H and  $H_0 \equiv H(U_0, V_0, X_0^1, \dots, X_0^n)$  is the value of H at the reference state  $(U_0, V_0, X_0^1, \dots, X_0^n)$ . Analogously,  $\hat{S}_0 \equiv \hat{S}(U_0, V_0, X_0^1, ..., X_0^n)$ .

In fact, one has

$$d L_Y \hat{S} = L_Y d\hat{S} = L_Y \frac{\omega}{f} = 0,$$
 (14)

being  $L_Y(\omega/f) = (L_Y \omega)/f - (\omega/f^2) (Y f) = 0$ . Then

$$L_Y \hat{S} = Y \hat{S} = q \tag{15}$$

where q is a constant. We can, without loss of generality, define another positive definite function H such that

$$\hat{S} \equiv \log(H). \tag{16}$$

Then we get that (15) is equivalent to the following equation for H:

$$Y H = q H, \tag{17}$$

which means that H is an homogeneous function of degree q. One has

$$d\hat{S} = \frac{dH}{H} = \frac{\omega}{f};\tag{18}$$

as a consequence,

$$dH = \frac{H}{f} \omega \tag{19}$$

which is an homogeneous of degree q closed Pfaffian form. Let us assume that  $q \neq 0$ , i.e., that H is not intensive. Then, from (A21) in Appendix A it follows

$$H = \frac{1}{q} \frac{H}{f} i_Y(\omega) = \frac{1}{q} H, \qquad (20)$$

which implies q = 1. The case q = 0 is treated in Appendix B, and it is excluded, H cannot be intensive. See also [17], where a more general proof is given.

The leaves  $\hat{S} = \text{const.}$  of the thermodynamic foliation coincide then with the leaves H = const. and H appears to play a privileged role in the construction of the thermodynamic foliation.

### **B.** metrical entropy S

We know that there exists a function H such that

$$\hat{S}(U, V, X^{1}, \dots, X^{n}) - \hat{S}(U_{0}, V_{0}, X^{1}_{0}, \dots, X^{n}_{0}) = \log\left(\frac{H(U, V, X^{1}, \dots, X^{n})}{H(U_{0}, V_{0}, X^{1}_{0}, \dots, X^{n}_{0})}\right)$$
(21)

where H is an extensive function. We have

$$\delta Q_{rev} = f \, d\hat{S} = \frac{f}{H} \, dH, \tag{22}$$

where f/H appears as a new integrating factor and H as extensive potential. By symmetry, the function H is suggested to be the thermodynamic potential one is looking for, i.e. the so-called metrical entropy [3], because one can write

$$\frac{f}{H} dH = dU + p \, dV - \sum_{i} \xi_i \, dX^i \tag{23}$$

where f/H is intensive as each coefficient of the Pfaffian form is, and H is extensive as each independent thermodynamic variable  $U, V, X^1, \ldots, X^n$  is. This identification of H with the metrical entropy is correct. We know, from the standard approach [3–7], that a metrical entropy has the property to be additive. In particular, the entropy Sof a system composed by two subsystems in thermal equilibrium is  $S = S_1 + S_2$ . Moreover, it is expected that the entropy of a system composed by n replicas of a subsystem  $\Sigma_0$  is  $S = n S_0$ , that is, it is extensive. We just have the extensivity property for H. Moreover, also on a statistical mechanical ground, S is required to be non-negative. Then, we can introduce on this ground the following assumption:

h5) We require that the metrical entropy S is extensive.

We can easily show that H is a metrical entropy because, up to a multiplicative constant, there exists only one extensive potential S and only one intensive integrating factor T such that  $\delta Q_{rev} = T \, dS$ ; as a consequence,  $f/H = (\partial H/\partial U)^{-1}$ plays the role of absolute temperature. The proof is the following. We have obtained

$$\omega = g \, dH,\tag{24}$$

where  $g \equiv f/H$  is homogeneous of degree zero. One may wonder if g and H are unique. By introducing another function G(H) we can obtain

$$\omega = \frac{g}{dG/dH} \, dG. \tag{25}$$

We want again the new integrating factor  $\bar{g} \equiv g/(dG/dH)$  to be homogeneous of degree zero and G to be homogeneous of degree one. Then we have

$$Y G = G \tag{26}$$

and

$$Y G(H) = \frac{dG}{dH} Y H = \frac{dG}{dH} H.$$
 (27)

Then

$$G = \frac{dG}{dH} H \tag{28}$$

which means

$$G = \gamma \ H \tag{29}$$

where  $\gamma$  is a constant. As a consequence, one finds

$$\frac{1}{\bar{g}} = \frac{\partial G}{\partial U} = \gamma \ \frac{\partial H}{\partial U} = \gamma \ \frac{1}{g}.$$
(30)

The entropy H and the absolute temperature g are then unique apart from a scale factor  $\gamma$  which can be fixed by fixing the absolute temperature scale [3].  $\hat{S}$  plays instead the role of empirical entropy [3]. We have found that, apart from a scale factor,

$$H \equiv S, \tag{31}$$

$$\frac{\partial H}{\partial U} \equiv \frac{1}{T} = \frac{H}{f} \tag{32}$$

The latter equality, together with the standard choice for T to be non-negative, justifies h4).

## C. corroboration from Gibbs' approach

 $\hat{S}$  can also be easily related to the standard definition of entropy also by simply appealing to Gibbs' approach. In fact, it is sufficient to consider the fundamental equation of thermodynamics in the entropy representation for an homogeneous system [14], which implies

$$T S = U + p V - \sum_{i} \xi_i X^i;$$
(33)

then

$$f = T S \tag{34}$$

this shows that f cannot identically vanish in thermodynamics, thus, a posteriori, the integrable Pfaffian form  $\delta Q_{rev}$  has to be non-dicritical, and the homogeneity symmetry has to be non-trivial (or transversal). Moreover,

$$d\hat{S} \equiv \frac{dS}{S} = d\log(S). \tag{35}$$

Of course, both (34) and (35) could be easily found at first sight from (9), but we have shown that on the ground of simple assumptions one can recover S and T as derived quantities without referring a priori to Gibbs' fundamental equation in the entropy representation.

We find that

$$\int_{S_0}^{S} \frac{dS}{S} = \int_{\Gamma} \frac{\omega}{f}.$$
(36)

As a consequence,

$$\hat{S} - \hat{S}_0 = \int_{\Gamma} \frac{\omega}{f} = \log(\frac{S}{S_0}) \tag{37}$$

and

$$S = S_0 \exp(\hat{S} - \hat{S}_0) \tag{38}$$

$$= S_0 \, \exp\left(\int_{\Gamma} \, \frac{\omega}{f}\right). \tag{39}$$

Notice that, a priori, one should write  $d\hat{S} = d \log(|S|)$ , and insert an absolute value in the argument of the logarithm in (37). In fact, from the point of view of classical thermodynamics, there is no constraint for S to be non-negative. Nevertheless, the left side of (36) has to be of definite sign, contrarily  $\hat{S}$  would not be well-defined where S = 0(the left side of (36) could still be defined as a principal value integral) and the thermodynamic foliation defined by  $\hat{S}$  would not be in a one-to-one correspondence with the one defined by S, because the map  $S \mapsto \hat{S}$  would not be injective.

From (37) we can also deduce that  $\hat{S}$  is not an homogeneous function, in fact a differentiable homogeneous function  $g(U, V, X^1, \ldots, X^n)$  of degree  $\alpha$  should satisfy  $Y = \alpha g$ . For  $\hat{S}$  we get

$$L_Y \,\hat{S} = Y \,\hat{S} = 1. \tag{40}$$

## D. positivity and concavity of entropy

It is interesting to notice that the thermodynamic entropy S is positive. There is no need of restricting the range of the metrical entropy S to positive values, because the thermodynamic potential H, which is realized to be a metrical entropy, is, by definition, positive definite. Of course, this agrees with the statistical mechanical approach. The classical ideal gas violates this property, in fact its entropy becomes negative and goes to  $-\infty$  as  $T \to 0$ ; but this behavior being corrected at low temperatures by quantum mechanics. [The positivity of S can be obtained in the framework we sketched in the previous subsection by recalling that, under the assumption h3),  $\hat{S}$  is required to be well-defined on each thermodynamic state belonging to the thermodynamic domain where the thermodynamic foliation is constructed; see the discussion in the previous subsection]. States such that S = 0 are singular and can be allowed to belong at most to the boundary of the thermodynamic domain, as we show in the following subsection.

As far as the concavity of the entropy is concerned, we limit ourselves to discuss how this fundamental stability requirement which is introduced in Gibbs' approach constraints the Pfaffian form  $\delta Q_{rev}$ . Concavity of S ensures that the system is thermodynamically stable [14]. We introduce then the assumption

# h6) We require that the metrical entropy S is concave.

Notice that the requirement of superadditivity for S would be equivalent, in fact superadditivity and homogeneity of S imply concavity [24,25]. Cf. also [17].

First, we underline that the concavity of S is not equivalent to the concavity of  $\hat{S}$ . From one hand, the concavity of S is a sufficient condition for the concavity of  $\hat{S}$ ; in fact, the logarithm of a concave function is a concave function (if g is a concave function and  $\phi$  is a concave non-decreasing function, then  $\phi \circ g$  is a concave function. The logarithm is a concave non-decreasing function). The concavity of S is not a necessary condition for the concavity of  $\hat{S}$  (if one considers  $S = \exp(-x^2)$ , which is not concave on  $\mathbb{R}$  but only for  $2x^2 - 1 < 0$ , one still obtains  $\hat{S} = -x^2$  which is concave on  $\mathbb{R}$ ). On the other hand, the concavity of  $\hat{S}$  does not ensure the concavity of S, because, in general is not true that the exponential of a concave function is concave (e.g., let us consider again  $\hat{S} = -x^2$ , which is a concave function on  $\mathbb{R}$ . The function  $S \equiv \exp(-x^2)$  is not concave on the whole real line).

The concavity of S can be obtained by imposing suitable conditions on the coefficients of the Pfaffian form  $\delta Q_{rev}$ . These conditions can be deduced from the standard ones on S [14]. Let us consider for simplicity S(U, V, N). We get

$$\frac{\partial S}{\partial U} = S \frac{1}{f} \tag{41}$$

$$\frac{\partial S}{\partial V} = S \frac{p}{f} \tag{42}$$

$$\frac{\partial S}{\partial U} = S \, \frac{-\mu}{f}.\tag{43}$$

The Hessian matrix for S is easily deduced to be

$$D^2 S \equiv \frac{S}{f^2} \begin{bmatrix} 1 - \frac{\partial f}{\partial U} & p - \frac{\partial f}{\partial V} & -\mu - \frac{\partial f}{\partial N} \\ p - \frac{\partial f}{\partial V} & p^2 + f \frac{\partial p}{\partial V} - p \frac{\partial f}{\partial V} & -\mu p + f \frac{\partial p}{\partial N} - p \frac{\partial f}{\partial N} \\ -\mu - \frac{\partial f}{\partial N} & -\mu p + f \frac{\partial p}{\partial N} - p \frac{\partial f}{\partial N} & \mu^2 - f \frac{\partial \mu}{\partial N} + \mu \frac{\partial f}{\partial N} \end{bmatrix}.$$

Concavity requires that all principal minors of odd order should be negative and all principal minors of even order should be positive. The Hessian determinant is zero because of the homogeneity of S. Then, in order to obtain a concave S one has simply to impose on the homogeneous integrable Pfaffian  $\delta Q_{rev}$  the following (necessary and sufficient) conditions involving the coefficients of the Pfaffian form and the integrating factor f:

$$1 - \frac{\partial f}{\partial U} < 0 \tag{44}$$

$$(1 - \frac{\partial f}{\partial U})(p^2 + f \frac{\partial p}{\partial V} - p \frac{\partial f}{\partial V}) - (p - \frac{\partial f}{\partial V})^2 > 0.$$
(45)

Notice that  $1 - \partial f / \partial U < 0$  amounts simply to  $\partial T / \partial U > 0$ , which is simply the positivity of the heat capacity at constant V, N.

# E. conditions for $\hat{S}$ and f to be globally defined

The homogeneity of the integrable non-dicritical Pfaffian form  $\delta Q_{rev}$  allows to find an integrating factor f whose expression holds globally by construction (by hypothesis,  $p(U, V, X^1, \ldots, X^n) \in C^1(\mathcal{D})$  and  $\xi_i(U, V, X^1, \ldots, X^n) \in C^1(\mathcal{D})$  for all  $i = 1, \ldots, n$ ). A priori it is not possible to ensure that also  $\hat{S}$  is defined everywhere, because singularities can arise where f = 0, i.e., if the set of zeroes of the integrating factor  $Z(f) = \{(U, V, X^1, \ldots, X^n) | f(U, V, X^1, \ldots, X^n) = 0\}$  is non-empty. In fact, where f vanishes  $\hat{S}$  can be not well-defined, as it is clarified in the following, in contrast with our requirement that the thermodynamic foliation is described by the potential  $\hat{S}$  in the convex set  $\mathcal{D}$ .

# 1. the set Z(f)

We know that  $f = TS \ge 0$ , and obviously  $Z(f) = Z(T) \cup Z(S)$ , where Z(T), Z(S) are the sets where T, S vanish respectively. Surely  $\hat{S}$  is not well-defined for each state belonging to Z(S), because of (37). Thus, one has to require that Z(S) belongs at most to the boundary of  $\mathcal{D}$ . This requirement is corroborated by the analysis of convex functions [26], in fact  $I \equiv -S$  is a convex function which attains its maximum value in Z(S) if  $Z(S) \neq \emptyset$  (recall that  $S \ge 0$ in our framework), and, in order that I is non-constant, it is necessary that Z(S) is contained in the boundary of the convex domain  $\mathcal{D}$  [cf. also [27], thm. C p. 124]. Z(T) is contained in the boundary as well (as it is evident if Tappears as independent variable). Then also Z(f) is contained in the boundary of the thermodynamic domain. Moreover,

# **h7**) We require that $Z(S) \subseteq Z(T)$ .

In the following discussion, we indicate with z collectively the independent thermodynamic variables. The assumption h7) is introduced because any state z such that  $T_z > 0$  and S(z) = 0 should belong to the boundary of the thermodynamic domain and should have the peculiar property to allow the system only to absorb heat along any non-adiabatic path  $\gamma_z$  starting from z in a neighborhood  $W_z$  of z. In fact, let us define the heat capacity along a path  $\gamma : [T_0, T] \to \mathcal{D}$  which does not include isothermal sub-paths:

$$C_{\gamma}(T) \equiv T \left(\frac{dS}{dT}\right)_{\gamma} = \omega(\dot{\gamma}). \tag{46}$$

If  $\gamma_z$  is a path starting from the state z, then

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

$$\tag{47}$$

should be positive for any state y non isoentropic to z in  $W_z$ , because S(y) > S(z) = 0, 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  $T_z > T_y$ ). [Heat absorption should occur also for any isothermal path starting from the state z, in fact  $Q = T_z \Delta S$  along an isothermal path and  $\Delta S > 0$ ]. Thermal contact with a colder body at  $T < T_z$  should allow an heat flow outgoing from the system (see also the discussion in Ref. [26]). Then, no quasi-static approximation of such a thermal contact can be allowed, no matter how near to  $T_z$  the temperature of the colder body could be, because, at least in a neighborhood of  $T_z$ , the system could only absorb heat. This behavior can be considered pathological, and the occurrence of the absolute minimum S = 0 of the thermodynamic entropy at T > 0 is refused in the framework of standard thermodynamics. As a consequence of the rejection of states with S = 0 at T > 0 one finds Z(f) = Z(T). Notice that in the classical ideal gas case, where S is allowed to become negative, one finds that  $Z(f) \supset Z(T)$  because T vanishes for U = 0 and S vanishes before the hypersurface U = 0 is reached.

Notice that h7) is automatically implemented if the boundary T = 0 is described by a (maybe even smooth) function  $U = b(V, X^1, \ldots, X^n)$  and conditions ensuring the continuity of S at T = 0 are allowed [26]. The function  $b(V, X^1, \ldots, X^n)$  can be construed as a ground-state energy. h7) can be substituted by the stronger assumption

 $\overline{\mathbf{h7}}$ ) We require that T = 0 is described by  $U = b(V, X^1, \dots, X^n)$ , where b is an extensive convex function defined on a convex cone  $\mathcal{K}_b$ , and that the domain  $\mathcal{D} \cup \partial \mathcal{D}$  coincides with the epigraph of b:

$$\mathcal{D} \cup \partial \mathcal{D} \equiv \operatorname{epi}(b) = \{ (U, V, X^1, \dots, X^n) \mid (V, X^1, \dots, X^n) \in \mathcal{K}_b, U \ge b(V, X^1, \dots, X^n) \}.$$
(48)

As a consequence, by defining the extensive coordinate  $B \equiv U - b(V, X^1, ..., X^n) \geq 0$  it is easy to show that  $Z(S) \subseteq Z(T)$ , because for an everywhere continuous entropy it holds

$$S(B, V, X^{1}, \dots, X^{n}) = S(0, V, X^{1}, \dots, X^{n}) + \int_{0}^{B} dY \frac{1}{T(Y, V, X^{1}, \dots, X^{n})},$$
(49)

where  $S(0, V, X^1, \ldots, X^n)$  is the value attained by S at B = 0 by continuity [all the matematical properties ensuring the existence of the improper integral  $\int_0^B dY \, 1/T$  are implicitly assumed]. See [26] for further details. Then we have Z(f) = Z(T). Notice that, if  $b \equiv 0$ , then  $\mathcal{D} \cup \partial \mathcal{D} = \mathcal{K} \times \overline{\mathbb{R}_+}$ , where  $\mathcal{K} \ni (V, X^1, \ldots, X^n)$  is a convex cone.

Then  $\hat{S}$  and S are defined everywhere, because  $\delta Q_{rev}/f$  is a closed Pfaffian form defined everywhere on  $\mathcal{D}$ . This solves the problem of ensuring the global existence of the integrating factor and of the potential, in particular, the entropy and the temperature are defined globally (about this problem in the frame of Carathéodory approach, cf. [9,10]).

We further introduce the following assumption:

h8) We require that to each level set S = const. corresponds a unique leaf.

In general, S is a submersion whose leaves are the connected components of  $S^{-1}(c)$ , where  $c \in \mathbb{R}_+$  is a constant. From a physical point of view, it is expected that each isoentropic surface S = c = const. is path-connected, in fact, given a state X and a state Y lying on the same isoentropic surface of an homogeneous thermodynamic system, it is physically mandatory that there exists an adiabatic reversible transformation [i.e. an adiabatic path] which connects X and Y. Thus, assumption h8) has to be ensured. In Appendix C we show a possible implementation of assumption h8).

It can be noted that the conditions  $\omega(Y) \neq 0$  and  $\omega(Y) = 0$  only on the boundary of the thermodynamic domain ensure that, given a fixed reference point  $z_0 \equiv (U_0, V_0, X_0^1, \dots, X_0^n)$ , the integral curve  $\gamma_{z_0}(t)$  of the vector field Y meets each leaf S = const. of the foliation if h8) is implemented, in fact  $S(\mathcal{D}) = (0, \infty)$  and it holds

$$(\gamma_{z_0}^*(t)S)(U_0, V_0, X_0^1, \dots, X_0^n) = S(\exp(t) \ U_0, \exp(t) \ V_0, \exp(t) \ X_0^1, \dots, X_0^n) = \exp(t) \ S(U_0, V_0, X_0^1, \dots, X_0^n).$$
(50)

Moreover, there exists only one intersection with each leaf. The given curve is then transverse with respect to the foliation.

Another physically well-grounded assumption is

**h9**) We require that  $\frac{\partial S}{\partial V}$  is positive.

This requirement means simply that the pressure p is positive definite.

# **F.** the problem of T = 0

This kind of approach is very interesting also from the point of view of the third law of thermodynamics [3–5,7,28]. A more complete analysis of this topic is the subject of Ref. [26,29]. We limit ourselves to a short summary of some points which have an evident link with the subject of this paper, referring the reader to Ref. [26,29] for details, for a general discussion and for also for complete references to the literature on the third law.

We assume that the T = 0 is a connected hypersurface (see also [26]), which coincides with the adiabatic boundary  $\delta Q_{rev} = 0$  of the thermodynamic domain, i.e.

**h10**) We require that T = 0 is a connected integral manifold of  $\delta Q_{rev}$ .

This means that, if  $\overline{h7}$ ) is implemented,  $U = b(V, X^1, \dots, X^n)$  has to be a solution of the Mayer-Lie system which is equivalent to the Pfaffian equation  $\omega = 0$  (see [12]), i.e. the following conditions

$$\frac{\partial U}{\partial V} = -p(U, V, X^1, \dots, X^n) = \frac{\partial b}{\partial V}$$
(51)

$$\frac{\partial U}{\partial X^i} = \xi_i(U, V, X^1, \dots, X^n) = \frac{\partial b}{\partial X^i} \quad \text{for } i = 1, \dots, n$$
(52)

have to be implemented. Then the function b has to be at least of class  $C^1(\mathcal{K}_b)$ .

Requirement h10) is not necessary if  $\overline{h7}$ ) is implemented and f and  $\omega$  are  $C^1$  everywhere (then b has to be of class  $C^2(\mathcal{K}_b)$ ). In fact, from  $f \ d\omega = df \wedge \omega$  one finds that the pull-back of the map  $F_b : \mathcal{D} \to \partial \mathcal{D}$ , where  $F_b^*(f) = f \circ F_b = 0$ , implements  $0 = F_b^*(df \wedge \omega) = F_b^*(df) \wedge F_b^*(\omega)$ . This implies that there exist a real function  $h \neq 0$  defined in  $\partial \mathcal{D}$  such that  $F_b^*(\omega) = h \ F_b^*(df)$  and  $F_b^*(df) = 0$  because  $F_b^*(f) = 0$ . Cf. also [20]. Under more general conditions on f and  $\omega$  it can be non-trivial that f = 0 is an integral manifold.

The use T as explicit independent coordinate is not suitable for studying the nature of the integral submanifold T = 0, in fact the Pfaffian form  $\delta Q_{rev}$  seems to be singular in T = 0 (the point is that the map  $U \mapsto T$  is not a diffeomorphism in T = 0). In order to avoid this problem the explicit use of U or B [or of another regular coordinate] is mandatory. We then use B explicitly. See also the discussion in [26,29]. Outside T = 0 [i.e. B = 0] there exists a thermodynamic foliation whose leaves are the hypersurfaces S = const. The nature of T = 0 is ambiguous, in the sense that it can correspond to a leaf of the thermodynamic foliation, the leaf T = 0, or it simply can correspond to an integral manifold of  $\delta Q_{rev}$  which is intersected by other integral manifolds of  $\delta Q_{rev}$ . In both cases,  $S : \mathcal{D} \to \mathbb{R}_+$  represents an at least  $C^2(\mathcal{D})$  submersion which generates the thermodynamic foliation at T > 0. We can show that the validity of the third law of thermodynamics can be related with the geometric nature of the integral submanifold T = 0.

In fact, under the hypothesis that the entropy S is concave and continuous at the surface T = 0, in the sense that there exists the limit as  $B \to 0^+$  of S for any finite value of the parameters  $V, X^1, \ldots, X^n$  [notice that the theory of convex functions allows to define S at T = 0, i.e. when U = b [26]], it can be shown that T = 0 corresponds to a special leaf of the thermodynamic foliation generated by the Pfaffian form  $\delta Q_{rev}$  if, and only if, the entropic version of the third law

$$\lim_{T \to 0^+} S = 0 \tag{53}$$

holds. We notice that Planck's restatement of the third law (53) is trivially mandatory for an homogeneous system, in fact  $\lim_{B\to 0^+} S(B,V,X^1,\ldots,X^n) = S_0$ , with  $S_0 > 0$  a positive constant, implies also that  $S_0 = \lim_{B\to 0^+} S(\lambda B, \lambda V, \lambda X^1, \ldots, \lambda X^n) = \lambda \lim_{B\to 0^+} S(B, V, X^1, \ldots, X^n) = \lambda S_0$ , which is possible only for  $S_0 = 0$ . It can also be noticed that the positivity and the concavity of S forces S to be finite as  $B \to 0$  [26]. In fact, the behavior of the convex function I = -S at the boundary has to be such that

$$\liminf_{x \to x_0} I(x) > -\infty \tag{54}$$

for any  $x \equiv (U, V, X^1, \dots, X^n)$  which converges to  $x_0 \equiv (U_0, V_0, X_0^1, \dots, X_0^n)$  belonging to the boundary of the convex domain [cf. problem F p. 95 of Ref. [27]]. Then a positive S has to be finite as  $T \to 0$ .

If (53) holds, then Z(S) = Z(T) and no leaf S = const. can intersect T = 0, in fact only the isoentropic surface S = 0 could intersect T = 0. If (53) is violated, and  $\lim_{B\to 0^+} S(B, V, X^1, \ldots, X^n) = S(0, V, X^1, \ldots, X^n)$ , then  $Z(S) \subset Z(T)$  and T = 0 is not a leaf; in fact, one can uniquely define the entropy to be  $S(0, V, X^1, \ldots, X^n)$  at  $(B = 0, V, X^1, \ldots, X^n)$ , and a peculiar intersection of adiabatic surfaces occurs [26]. The main point is that, if (53) is violated, a state belonging to the set Z(T) can also belong to an isoentropic surface intersecting T = 0, and there are two adiabatic paths starting from that state, one contained in T = 0 and the other contained in the aforementioned isoentropic surface. This happens as a consequence of the fact that the surface  $S = S(0, V, X^1, \ldots, X^n) = \text{const.} > 0$ , if  $(0, V, X^1, \ldots, X^n)$  is not a local minimum of S, necessarily intersects the graph of S along a codimension one submanifold which is connected to the submanifold T = 0. [The proof is found in [26]; see also [29]]. This means that the integral manifold  $S = S(0, V, X^1, \ldots, X^n)$  then each point  $(0, \lambda, V, \lambda, X^1, \ldots, \lambda, X^n)$  belonging to the cone of  $(0, V, X^1, \ldots, X^n)$  is such that  $S(0, \lambda, V, \lambda, X^1, \ldots, \lambda, X^n) = \lambda S(0, V, X^1, \ldots, X^n)$  and it is not a local minimum as

well [the proof is trivial]. Then, each (would-be) leaf S = const. intersects T = 0. One does not obtain a well-defined thermodynamic foliation if T = 0 is included, actually a foliation can be obtained in this case only if zero-measure set represented by the surface T = 0 is excised from the thermodynamic domain. Contrarily, one obtains a foliation except for a zero-measure set represented by the surface T = 0, i.e. the inner part of the thermodynamic domain is foliated into surfaces S = const., and locally the adiabatic inaccessibility holds, but these (would-be) leaves are actually connected by the adiabatic surface T = 0 and the adiabatic inaccessibility is violated, even if only along special curves reaching T = 0 [26]. Note that the failure of the Lipschitz property for ordinary differential equation for adiabatic curves starting at T = 0 is related to the singular behavior of the thermodynamic foliation at T = 0when (53) is violated [26]. Note also that, on the ground of assumption h8), when (53) is violated one has to impose that any point  $(0, V, X^1, \ldots, X^n)$  which is a local minimum has to be also a global minimum (contrarily, h8) would be violated).

If, instead, T = 0 is a leaf, then no leaf S = const. is allowed to reach T = 0. Leaves S = const. can at most asymptotically approach T = 0, but no one can be extended therein. (53) has to hold for a continuous S because the limit of S as  $T \to 0$  cannot depend on the parameters  $V, X^1, \ldots, X^n$  (otherwise T = 0 is not a leaf) [26,29].

Note that also the approach discussed herein is able to make immediately evident the necessity of the discussion of the states which belong to Z(f), i.e., as a consequence of h7), of the states which belong to Z(T). The third law has to be discussed in the framework of thermodynamic formalism, and the validity of (53) emerges as a "regularity" condition on the boundary T = 0 for the differential equation  $\delta Q_{rev} = 0$  of thermodynamics, in particular it appears as a condition which has to be imposed if a foliation of the whole thermodynamic domain (including T = 0) has to be obtained.

In the framework of our approach, (53) holds if and only if, whichever path  $\gamma^0$  is chosen in approaching T = 0 and having a point belonging to T = 0 as its final point, the integral of the form  $\delta Q_{rev}/f$  diverges to  $-\infty$ . The condition is clearly necessary, because (53) implies the divergence of (37); its sufficiency is also evident, being equivalent to  $\log(S) \to -\infty$ . Notice that this condition on the integral of  $\omega/f$  does not require to define the entropy at T=0.

Moreover, it is easy to show that a sufficient condition for (N) to hold is  $\omega \in C^1$  everywhere [i.e. also on the boundary T = 0, which implies  $f \in C^1$  everywhere. In fact, one has

$$\frac{\partial f}{\partial U} = 1 + S \frac{\partial T}{\partial U} \tag{55}$$

which has to be finite at T = 0; it holds  $\partial T / \partial U = 1 / C_{X^1, \dots, X^{n+1}}$ , where  $C_{X^1, \dots, X^{n+1}}$  is the standard heat capacity, which has to vanish in the limit as  $T \to 0$  because S has to be finite in that limit. As a consequence,  $\partial T/\partial U =$  $1/C_{X^1,\ldots,X^{n+1}} \to \infty$  as  $T \to 0^+$ , thus (55) is finite only if  $S \to 0$  as  $T \to 0^+$ . Further details and conditions are the subject of forthcoming papers [26,29].

## G. a note on the reference state

The reference state  $(U_0, V_0, X_0^1, \ldots, X_0^n)$  has to satisfy a constraint which is trivial but its discussion can be physically interesting. From the point of view of thermodynamics, given a system described by three variables (U, V, N), reference states like (0,0,0) or (0,V,0) are meaningless. In fact, they correspond to the absence of the system under study. Statistical mechanics provides a criterion for obtaining a meaningful thermodynamic description: there should be a statistically relevant number of elementary constituents (atoms, molecules, particles) of the system. In particular, the thermodynamic limit is well-known to be the tool allowing to find out thermodynamics from statistical mechanics. [See also [17]]. N = 0 correspond to the absence of constituents. Without necessarily referring to the above statistical mechanical suggestion, one may wonder when a thermodynamic description starts being available. The system should be such that thermodynamic fluctuations allow to define meaningful macroscopic variables; moreover, the system under study should be realized to be involved with appropriate thermodynamic properties. In other terms, a "preparation" procedure of the system, in such a way that a macroscopic description becomes available and a set of relevant thermodynamic variables can be identified, should be considered as a preliminary condition to the thermodynamic description.

### H. fundamental equation and homogeneous Pfaffian form

It is known that the fundamental equation contains all the relevant thermodynamic information about the system by construction [14]. In order to determine the fundamental equation S by integration of the Pfaffian form  $\delta Q_{rev}$ , it is necessary to consider the Pfaffian form  $\delta Q_{rev}$  representing a sufficiently general thermodynamic transformation which can be implemented with the system under study. Before clarifying what we mean by "sufficiently general", let us discuss some examples. In the case of the classical ideal gas, one should consider the system as open and let the extensive variables U, V, N to appear in  $\delta Q_{rev}$ . As it is easy to show, by considering  $\delta Q_{rev}$  with N = const. (closed system) leads to a wrong fundamental equation, to be compared with the correct one displayed in Ref. [14]. If a photon gas is studied, only two variables are necessary, U, V, whereas N is not a good parameter [which is related to the fact that the number of particles is not a good observable for a massless particles gas]. These examples show that neglecting some variable one would find incorrect results. Moreover, the relevant extensive variables should be settled out by considering, for each system, its own macroscopic features. Let us suppose that a system can be consistently described, when e.g. insulated, by means of three extensive variables U, V, N appearing in the fundamental equation S(U, V, N). This does not exclude a priori the possibility to consider the system in a more general situation in which the system is under the influence e.g. of some external field which could give rise to new thermodynamic features as a paramagnetic gas under the influence of an external magnetic field, one could introduce an external magnetic field  $\vec{B}_e$  and the magnetization  $\vec{M}$  as in Ref. [14]]. Then one can allow an extension of the thermodynamic space, by enlarging the set of the extensive variables, e.g. by passing from U, V, N to U, V, N, X, where X is the new extensive variable which can assume the value X = 0 and whose conjugate intensive variable is  $\xi$ . A new fundamental equation  $\overline{S}(U, V, N, X)$  is obtained, which, by continuity, reduces to S(U, V, N) when X = 0:  $\overline{S}(U, V, N, X = 0) = S(U, V, N)$ . Of course, an enlarged set of integrability conditions should be verified [cf. eqn. (59) in the next section]. A consistency condition for such an extension to hold consists in requiring that  $\xi(U, V, N, X = 0) = 0$ . This can be easily realized if one refer to the Massieu potentials which are obtained by performing a Legendre transformation of the fundamental equation [14]. If  $\phi(1/T, p/T, \mu/T, \xi/T)$  is the Massieu potential associated with S in which only intensive variables appear, then, in order to obtain a consistent reduction of thermodynamic degrees of freedom by posing X = 0, it is necessary to put  $\xi = 0$ .

Then "sufficiently general" means that in the expression of the Pfaffian form  $\delta Q_{rev}$  one takes into account all the extensive variables which cannot be consistently set equal to zero. This kind of approach to the problem of the construction of the fundamental equation appears to be more realistic than the one requiring to refer to the Pfaffian form  $\delta Q_{rev}$  corresponding to the most general transformation the system could be allowed to perform [the most general transformation is hardly known]. An explicit construction of this kind occurs in black hole thermodynamics, and it is discussed in Ref. [17]. Because of the presence of gravity, thermodynamics is no more homogeneous, but a quasi-homogeneous symmetry of the Pfaffian form  $\delta Q_{rev}$  can still be identified [17]. We point out also that quasi-homogeneity is the natural symmetry for standard thermodynamics when one or more independent variables are intensive [30].

### IV. COMPARISON WITH THE STANDARD APPROACH

In the standard approach to homogeneous systems, in the so-called entropy representation, it is known that the knowledge of the fundamental equation is equivalent to the knowledge of the so-called state equations [14]. In particular, we have the following general scheme for reconstructing the fundamental equation of thermodynamics from the state equations [14]. This method is equivalent to the one we propose, where we know the intensive variables  $p, \xi_1, \ldots, \xi_n$  and we reconstruct S. Given a system described by n+2 extensive variables, it is sufficient to know n+1 state equations, i.e. n+1 intensive functions (pressure, chemical potential,...) in order to reconstruct the (n+2)-esime state equation within an additive constant, and, then, to reconstruct the fundamental equation. In fact, being S an homogeneous function of degree one of the extensive variables, one has

$$S = \frac{1}{T}U + \frac{p}{T}V - \sum_{i}\frac{\xi_i}{T}X^i;$$
(56)

moreover, by differentiating the above formula for S, the Gibbs-Duhem equation follows, which allows to reconstruct the (n + 2)-esime state equation from the other ones:

$$U d\left(\frac{1}{T}\right) + V d\left(\frac{p}{T}\right) - \sum_{i} X^{i} d\left(\frac{\xi_{i}}{T}\right) = 0.$$
(57)

Here, we assume to know  $p, \xi_1, \ldots, \xi_n$  and we can recover T (within an integration constant) from the knowledge of  $p, \xi_1, \ldots, \xi_n$ . Then we can reconstruct S. Of course, in general such a reconstruction of the (n + 2)-esime state equation is possible only under suitable integrability conditions to be satisfied by  $p, \xi_1, \ldots, \xi_n$ . These integrability conditions coincide with the integrability conditions of  $\delta Q_{rev}$ . A Pfaffian form

$$\omega = \sum_{i} \omega_i \, dx^i \tag{58}$$

is integrable if it satisfies the integrability condition  $\omega \wedge d\omega = 0$ , that is, if, for any i, j, k

$$l_{ijk} = \omega_i \left( \frac{\partial \omega_j}{\partial x^k} - \frac{\partial \omega_k}{\partial x^j} \right) + \omega_j \left( \frac{\partial \omega_k}{\partial x^i} - \frac{\partial \omega_i}{\partial x^k} \right) + \omega_k \left( \frac{\partial \omega_i}{\partial x^j} - \frac{\partial \omega_j}{\partial x^i} \right) = 0.$$
(59)

[See e.g. Ref. [3]]. These conditions have to be satisfied by (1). E.g., in the case of three variables U, V, N, one has

$$l_{UVN} = \frac{\partial p}{\partial N} + \frac{\partial \mu}{\partial V} + \mu \frac{\partial p}{\partial U} - p \frac{\partial \mu}{\partial U} = 0.$$
(60)

These conditions ensure that  $\delta Q_{rev}/f$  is an exact differential. Let us consider the Gibbs-Duhem equation in which T is unknown

$$d \log\left(\frac{1}{T}\right) = -\frac{V \, dp - \sum_i X^i \, d\xi_i}{U + p \, V - \sum_i X^i \, \xi_i} = -\frac{V \, dp - \sum_i X^i \, d\xi_i}{f};\tag{61}$$

the integrability conditions ensure that (61) has a right member which is an exact differential, as can be easily verified. In fact, let us consider

$$\frac{\delta Q_{rev}}{f} = \frac{dU + p \, dV - \sum_i \, \xi_i \, dX^i}{f} = \frac{df}{f} - \frac{V \, dp - \sum_i \, X^i \, d\xi_i}{f};\tag{62}$$

it is evident that  $d\hat{S} = \delta Q_{rev}/f$  holds if and only if

$$\frac{V\,dp - \sum_i \,X^i\,d\xi_i}{f} \tag{63}$$

is the differential of a function. Moreover, from f = T S and from

$$d\hat{S} = \frac{df}{f} - \frac{V \, dp - \sum_i X^i \, d\xi_i}{f} = \frac{dS}{S} \tag{64}$$

the Gibbs-Duhem equation (61) follows. Note that the Gibbs-Duhem equation (61) allows to find  $\log(1/T)$  within an additive constant, which means that T is determined within a multiplicative constant, and also S is determined within a multiplicative constant. In in this respect, the integration of  $\omega/f$  and the integration of (61) are equivalent. As a counter-example where the integrability conditions fail, let us consider  $\delta Q_{rev} = du + pdV - \mu dN$ , with p = U/Vand  $\mu = UV/N^2$ . The integrability condition (60) is not satisfied, in fact  $l_{UVN} = U/N^2 \neq 0$ . One has

$$d \log\left(\frac{1}{T}\right) = \frac{V-N}{U(2N-V)} dU + \frac{V+N}{2N-V} dV - \frac{2V}{N(2N-V)} dU$$
$$\equiv a_U dU + a_V dV + a_N dN.$$

The right member is not an exact differential, because e.g.  $\partial_V a_U = N/U(2N-V)^2 \neq \partial_U a_V = 0$ . About the Gibbs-Duhem equations see also [17] and [30].

### A. densities

We introduce the so called *densities*. One defines density the ratio of the extensive independent variables with respect to one of them. For example, it is possible to define:

$$\begin{split} u &\equiv U/V \\ x^i &\equiv X^i/V. \end{split}$$

The n + 1 densities so obtained are the physical degrees of freedom in the case of an homogeneous substance. Then the fundamental equation in the entropy representation becomes

$$S(U, V, X^{1}, \dots, X^{n}) = V \ s(u, x^{1}, \dots, x^{n}),$$
(65)

where

$$s(u, x^{1}, \dots, x^{n}) = \frac{1}{T} u + \frac{p}{T} - \sum_{i} \frac{\xi_{i}}{T} x^{i},$$
(66)

where the intensive variables are now functions of  $u, x^1, \ldots, x^n$ . The Gibbs-Duhem equation becomes

$$u d\left(\frac{1}{T}\right) + d\left(\frac{p}{T}\right) - \sum_{i} x^{i} d\left(\frac{\xi_{i}}{T}\right) = 0$$

$$(67)$$

and now only intensive variables appear.

In the approach by means of the homogeneous differential form  $\delta Q_{rev}$ , the use of the densities leads easily to the following result:

$$\delta Q_{rev} = (u + p - \sum_{i} \xi_i x^i) \, dV + V \, (du - \sum_{i} \xi_i \, dx^i).$$
(68)

Then, we get

$$\frac{\delta Q_{rev}}{f} = \omega_0 + \frac{dV}{V},\tag{69}$$

where

$$\omega_0 \equiv \frac{du - \sum_i \xi_i \, dx^i}{u + p - \sum_i \xi_i \, x^i} = \frac{ds}{s}.$$
(70)

Notice that in the latter approach both s and T are unknown. All the intensive variables  $p, \xi_1, \ldots, \xi_n$  are to be known if the entropy has to be determined, thus p has to be known in order that the fundamental equation can be recovered. This is completely in agreement with what happens in the standard approach, where only one intensive variable is allowed to be unknown [it can be reconstructed by means of the Gibbs-Duhem equation]. One may wonder why in the case of an homogeneous one-component system one can sometimes recover the fundamental equation S(U, V, N)without any knowledge of the chemical potential  $\mu$ . The point is that, by passing to the densities with respect to N [indicated again with u, v], one has S = N s(u, v) and

$$dS = \frac{dU + p \, dV - \mu \, dN}{T} = \frac{1}{T(u, v)} \, N \left( du + p(u, v) \, dv \right) + \frac{1}{T(u, v)} \, \left( u + p(u, v) \, v - \mu(u, v) \right) \, dN \tag{71}$$

$$= N \frac{du + p(u, v) dv}{T(u, v)} + \frac{u + p(u, v) v - \mu(u, v)}{T(u, v)} dN$$
(72)

$$= N \, ds + s \, dN. \tag{73}$$

Then, it is possible to find s(u, v) by considering the system as closed if the temperature T(u, v) is known. The point is that it is legitimate to ignore  $\mu$  only if the dependence of the temperature on u, v is known. A typical example of such a system where T is known is represented by the classical ideal gas [14].

#### V. CONCLUSIONS

In this paper we have shown that, by choosing the extensive variables  $(U, V, X^1, \ldots, X^n)$  as independent variables, the integrability and the homogeneity of  $\delta Q_{rev}$  allow to find explicitly and immediately an integrating factor for  $\delta Q_{rev}$ . The relation between the potential  $\hat{S}$  and the entropy S is straightforward. It is to be noted that the entropy S arising from this calculation corresponds to the fundamental equation in the entropy representation. Thus our approach allows to find a direct link between Carathéodory approach, based on differential forms, and Gibbs one, based on the postulate of the concavity and homogeneity of the entropy  $S(U, V, X^1, \ldots, X^n)$ . The role of the homogeneity as a symmetry for the system and as a tool for constructing the thermodynamic formalism has been enhanced.

# APPENDIX A: INTEGRABLE HOMOGENEOUS PFAFFIAN FORM

Here we sketch a more elementary proof for some statements appearing in sect. I. Let us consider an homogeneous Pfaffian form in three variables (the generalization to n > 3 variables is straightforward):

$$\omega = P \, dx + Q \, dy + R \, dz,\tag{A1}$$

where P, Q, R are homogeneous functions of degree k (non necessarily k integer) in x, y, z:

$$(x\partial_x + y\partial_y + z\partial_z) P = k P; (A2)$$

$$(x\partial_x + y\partial_y + z\partial_z) Q = k Q;$$
(A3)

$$(x\partial_x + y\partial_y + z\partial_z) R = k R.$$
(A4)

The Liouville vector field is  $Y \equiv (x\partial_x + y\partial_y + z\partial_z)$ . The integrability condition is

$$P\left(\partial_z Q - \partial_y R\right) + Q\left(\partial_x R - \partial_z P\right) + R\left(\partial_y P - \partial_x Q\right) = 0.$$
(A5)

Then an integrating factor for  $\omega$  is given by

$$\mu \equiv P \ x + Q \ y + R \ z,\tag{A6}$$

provided that  $\mu \not\equiv 0$ . Let us check that

$$\omega_e \equiv \frac{\omega}{\mu} \tag{A7}$$

is closed. We have to check the equality of the mixed derivatives, that is, we have to verify that

$$\partial_z \left(\frac{P}{\mu}\right) = \partial_x \left(\frac{R}{\mu}\right) \tag{A8}$$

$$\partial_y \left(\frac{P}{\mu}\right) = \partial_x \left(\frac{Q}{\mu}\right) \tag{A9}$$

$$\partial_x \left(\frac{Q}{\mu}\right) = \partial_y \left(\frac{R}{\mu}\right).$$
 (A10)

We verify explicitly only (A8). We have

$$\partial_z \left(\frac{P}{\mu}\right) = \frac{1}{\mu} \partial_z P - \frac{P}{\mu^2} \left(x \partial_z P + y \partial_z Q + z \partial_z R + R\right)$$
(A11)

$$= \frac{1}{\mu^2} \left( Q \ y \ \partial_z \ P + R \ z \ \partial_z \ P - P \ y \ \partial_z \ Q - P \ z \ \partial_z \ R + P \ R \right).$$
(A12)

Analogously, we get

$$\partial_x \left(\frac{R}{\mu}\right) = \frac{1}{\mu^2} \left(P \ x \ \partial_x \ R + Q \ y \ \partial_x \ R - R \ x \ \partial_x \ P - R \ y \ \partial_x \ Q - P \ R\right). \tag{A13}$$

We have to show that

$$(Q \ y \ \partial_z \ P + R \ z \ \partial_z \ P - P \ y \ \partial_z \ Q - P \ z \ \partial_z \ R + P \ R) -(P \ x \ \partial_x \ R + Q \ y \ \partial_x \ R - R \ x \ \partial_x \ P - R \ y \ \partial_x \ Q - P \ R) = 0.$$
(A14)

We obtain

$$y Q (\partial_x R - \partial_z P) - R (x \partial_x P + z \partial_z P) - R y \partial_y Q$$
  
+P (x \overline{\overline{A}}\_x R + z \overline{\overline{A}}\_z R) + P y \overline{\overline{A}}\_z Q = 0. (A15)

The homogeneity of P, R allows to modify the second and the fourth term above

 $y Q (\partial_x R - \partial_z P) + R y \partial_y P - k P R - R y \partial_y Q$ 

$$-P y \partial_y R + k P R + P y \partial_z Q = 0.$$
(A16)

This can rewritten as follows

$$y \left[ P \left( \partial_z Q - \partial_y R \right) + Q \left( \partial_x R - \partial_z P \right) + R \left( \partial_y P - \partial_x Q \right) \right] = 0.$$
(A17)

Because of the integrability condition (A5), the term appearing in the square parentheses is zero, and the proof is completed. This proof is an extension to the case of three variables of the proof appearing in Ref. [23], p. 19. It is also interesting to note that, an analogous generalization of Ref. [23], p.18-20, allows to show that, if the coefficients

 $P/\mu, Q/\mu, R/\mu$  of the 1-form  $\omega_e$  appearing in (A7) are homogeneous of degree  $\alpha \neq -1$ , so that  $\omega_e$  is an exact 1-form of degree  $\alpha + 1$ , then the solutions of the equation  $\omega_e = 0$  are

$$g = \text{const.}$$
 (A18)

where

$$g \equiv \frac{1}{\alpha+1} \left( x \, \frac{P}{\mu} + y \, \frac{Q}{\mu} + z \, \frac{R}{\mu} \right) \tag{A19}$$

is an homogeneous function of degree  $\alpha + 1$  which satisfies

$$\omega_e = dg. \tag{A20}$$

In fact, one easily finds that the potential associated with  $\omega_e$  is given by

$$g = \frac{1}{\alpha + 1} i_Y(\omega_e) \tag{A21}$$

[proof:  $(\alpha + 1) dg = d i_Y(\omega_e) = -i_Y d\omega_e + L_Y \omega_e = L_Y \omega_e = (\alpha + 1) \omega_e$ ]. If, instead,  $\alpha = -1$ , then the solutions of  $\omega_e = 0$  have to be found by quadratures [23].

# APPENDIX B: FURTHER NOTES ON THE INTEGRAL OF $\omega/\mu$

Let us assume that

$$\omega_{(k+1)} \equiv \sum_{i=1}^{n} P_i \, dx^i \tag{B1}$$

is an homogeneous integrable Pfaffian form of degree k + 1, with  $P_i$  homogeneous of degree k for all i = 1, ..., n. The Liouville operator is

$$Y = \sum_{i=1}^{n} x^{i} \frac{\partial}{\partial x^{i}}.$$
 (B2)

 $\mathbf{If}$ 

$$\mu = \sum_{i=1}^{n} x^{i} P_{i} \tag{B3}$$

is the corresponding integrating factor, then

$$d\hat{W} \equiv \frac{\omega_{(k+1)}}{\mu} = \frac{dW}{W} \tag{B4}$$

where W > 0 is defined by  $\hat{W} = \log(W)$ . Moreover, we know that W has to be an homogeneous function of degree q, because  $dL_Y \hat{W} = L_Y d\hat{W} = 0$ . We then find

$$dW = \sum_{i=1}^{n} (\partial_i W) \, dx^i = \frac{W}{\mu} \, \sum_{i=1}^{n} \, P_i \, dx^i, \tag{B5}$$

thus one has

$$(\partial_i W) = \frac{W}{\mu} P_i \quad \forall i = 1, \dots, n.$$
(B6)

As a consequence, one obtains

$$Y W = \sum_{i=1}^{n} x^{i} (\partial_{i} W) \tag{B7}$$

$$=\sum_{i=1}^{n} x^{i} \frac{W}{\mu} P_{i} \tag{B8}$$

$$= q W. (B9)$$

From (B3) one finds

$$\sum_{i=1}^{n} x^{i} \frac{W}{\mu} P_{i} = W$$
(B10)

thus the only allowed value for q is q = 1. If q = 0, one would get W = 0 everywhere, which is absurd. Then W is homogeneous of degree one (extensive function). One then has  $\omega_{(k+1)} = g_{(k)} dW$ , where  $g_{(k)}$  is homogeneous of degree k.

We show that, if G is an homogeneous function of degree q such that

$$\omega_{(k+1)} = g_{(k+1-q)} \, dG,\tag{B11}$$

where  $g_{(k+1-q)}$  is homogeneous of degree k+1-q, then necessarily

$$G = \zeta W^q, \tag{B12}$$

where  $\zeta = \text{const.}$  In fact, one has

$$\omega_{(k+1)} = g_{(k+1-q)} \, dG = g_{(k)} \, dW \tag{B13}$$

and

$$g_{(k+1-q)} = \frac{g_{(k)}}{dG/dW}.$$
 (B14)

Moreover, the homogeneity of G(W) implies

$$D G = q G = \frac{dG}{dW} W, \tag{B15}$$

that is,

$$\frac{dG}{dW} = q \frac{G}{W},\tag{B16}$$

whose solution is (B12).

Notice that q = 1 is a consequence of the construction of the integrating factor  $\mu$ . In fact, one could find another integrating factor  $\bar{\mu} = \mu/q$ . The corresponding potential would be then  $G = W^q$ .

### **APPENDIX C: IMPLEMENTATION OF ASSUMPTION H8)**

Let us assume that assumption  $\overline{h7}$  holds and use the variable  $B \equiv U - b(V, X^1, \ldots, X^n)$ . We then have  $\mathcal{D} = (0, \infty) \times \mathcal{K}_b$ . We further assume that the third law (53) holds and that  $\lim_{U\to\infty} S(U, V, X^1, \ldots, X^n) = +\infty$  for all fixed  $(V, X^1, \ldots, X^n) \in \mathcal{K}_b$ . The latter hypothesis is reasonable [notice that it does not hold for systems which allow negative temperatures]. Then, for each positive constant  $c \in \mathbb{R}_+$ , one finds for all fixed  $(V, X^1, \ldots, X^n) \in \mathcal{K}_b$ 

$$\lim_{B \to 0^+} \left( S(B, V, X^1, \dots, X^n) - c \right) = -c < 0 \tag{C1}$$

$$\lim_{B \to +\infty} (S(B, V, X^1, \dots, X^n) - c) = +\infty.$$
(C2)

Then, a variant of the implicit function theorem [31] shows that there exists a unique function  $B_c(V, X^1, \ldots, X^n) : \mathcal{K}_b \to (0, \infty)$  such that  $S(B_c(V, X^1, \ldots, X^n), V, X^1, \ldots, X^n) - c = 0$ . This function is continuous (actually  $C^2$ ) and it defines the unique leaf corresponding to  $S^{-1}(c)$ .

[Sketch of proof: Let us put  $Y \equiv V, X^1, \ldots, X^n$  in the following. Then  $Y \in \mathcal{K}_b$ . S is continuous and monotonically strictly increasing in B, hence also the function  $\sigma_c(B,Y) \equiv S(B,Y) - c$  has these properties. In particular,  $\sigma_c(B,Y)$  is continuous as a function of B for any fixed  $Y \in \mathcal{K}_b$ . Permanence of the sign implies that there exist two real numbers  $b_1 < b_2$  such that  $\sigma_c(b_1, Y) < 0 < \sigma_c(b_2, Y)$  for all  $Y \in \mathcal{K}_b$ . Then, from the intermediate value theorem it follows that there exists a value  $\bar{b} \in (b_1, b_2)$  such that  $\sigma_c(\bar{b}, Y) = 0$  for any fixed  $Y \in \mathcal{K}_b$ . Monotonicity ensures that  $\bar{b}$  is unique. The function  $B_c(Y)$  is then defined as the map  $B_c(Y) = \bar{b}$  for each fixed  $Y \in \mathcal{K}_b$ . This function is also continuous. In fact, the set  $Z(\sigma_c) \equiv \{(B,Y) | \sigma_c(B,Y) = 0\}$  is a closed set, being  $\sigma_c$  a continuous function. Given a sequence  $\{Y_n\} \subseteq \mathcal{K}_b$  such that  $\lim_{n\to\infty} Y_n = Y_0 \in \mathcal{K}_b$ , one has  $(B_c(Y_n), Y_n) \in Z(\sigma_c)$  and, moreover,  $(\lim_{n\to\infty} B_c(Y_n), \lim_{n\to\infty} Y_n) \in Z(\sigma_c)$ , being  $Z(\sigma_c)$  closed.  $\lim_{n\to\infty} B_c(Y_n) = B_c(Y_0)$  then follows.]

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