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The Concavity of Entropy and Extremum Principles in Thermodynamics

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We revisit the concavity property of the thermodynamic entropy in order to formulate a general proof of the minimum energy principle as well as of other equivalent extremum principles that are valid for thermodynamic potentials and corresponding Massieu functions under different constraints. The current derivation aims at providing a coherent formal framework for such principles which may be also pedagogically useful as it fully exploits and highlights the equivalence between different schemes. We also elucidate the consequences of the extremum principles for the general shape of thermodynamic potentials in relation to first-order phase transitions.

KEY WORDS: Equilibrium thermodynamics; entropy concavity; maximum entropy principle; thermodynamic representation theory.

1. INTRODUCTION

In developing the formal structure of thermodynamics, one usually starts from the maximum entropy principle as the guiding principle that is used to predict the equilibrium conditions which apply to isolated systems. This is, actually, the way the subject was introduced by Callen in his celebrated book.(1) Crucially important in his presentation of equilibrium thermodynamics is the proof of the equivalence between different representations which are based on different choices of the natural variables that can be introduced in order to describe the macroscopic state of the system. Such a proof implies an extension of the extremum principle to other thermodynamic schemes. However, the approach that is usually pursued to justify the above equivalence, albeit physically well founded, may be not

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completely satisfactory on the formal side. More specifically, the ordinary proof of the minimum energy principle is formulated for a system with just one degree of freedom and its extension to a thermodynamic space of higher dimensionality is not, in our opinion, straightforward.

This state of affairs is also probably responsible for the somewhat uncertain status of "thermodynamic potentials" with multiple minima that are usually introduced when discussing first-order phase transitions.(1) Actually, it is not immediately clear how such a potential, which fails to fulfil the convexity requirement, is related to the fundamental equation of the system, unless one explicitly intends to represent a Landau free energy, i.e., the outcome of a mean-field calculation.

For the above reasons, we believe that it can be useful to revisit the proof of the extremum principles used in thermodynamics in order to place all representations on a more clear mathematical basis which may turn useful also for a pedagogical presentation of the subject.

The outline of the paper is as follows: in Section 2, we provide a general proof of the minimum energy principle based on the concavity property of the entropy function. Then, upon discussing the case of a system in contact with a reservoir, we derive in Section 3 other forms of the extremum principle which apply to the generalized thermodynamic potentials and related Massieu functions. We also analyze the pattern of singularities of, say, the Gibbs free energy in proximity to a first-order transition point. Some further remarks and a brief summary of the main results are given in the Conclusions.

2. THE MINIMUM ENERGY PRINCIPLE

Following Callen,(1) the fundamental problem of thermodynamics is to find the equilibrium state of an *overall isolated* macroscopic system following the removal of one or more internal constraints, i.e., walls restrictive with respect to the exchange of energy and, possibly, of other extensive quantities between the various parts of the system. As is well known, the solution to this problem can be cast in terms of the maximum entropy principle: the equilibrium state eventually singled out by the system is the one that maximizes the total entropy out of the variety of states that are compatible with the residual constraints.

Thermodynamics essentially postulates three properties for the entropy S:(1) (1) S is a well-behaved, first-order homogeneous function of the extensive parameters (a property leading to Euler's theorem (1)); (2) S is additive over disjoint subsystems; and (3) the partial derivative of S with respect to the energy U is strictly positive (implying that the temperature $T > 0$). In particular, this latter condition allows one to express the energy as a function of the entropy as well as of the other extensive parameters X_i which specify the state of the system, in such a way that the knowledge of $U(S, X_1, X_2,...)$ is equivalent to that of $S(U, X_1, X_2,...)$. In the following, we shall ignore any exception to the above conditions such as those arising from the existence of long-ranged interactions between the constituent particles (additivity and, possibly, extensivity violated), or from an effective ergodicity breaking (which causes the unattainability of equilibrium).

In order to set the stage for our subsequent reasoning, we consider an isolated system described by the energy U, the volume V, and the number of particles N as the only extensive parameters. For this system, the entropy is written as

$$S(U, V, N) = S_U(U, V, N)\, U + S_V(U, V, N)\, V + S_N(U, V, N)\, N, \tag{1}$$

where $S_X(\cdots)$ is the partial derivative of S with respect to X and $S_U(U, V, N) > 0$. This condition allows one to solve Eq. (1) in U,

$$U(S, V, N) = T(S, V, N)\, S - P(S, V, N)\, V + \mu(S, V, N)\, N, \tag{2}$$

where $T(S, V, N) \equiv U_S(S, V, N)$ is the temperature, $P(S, V, N) \equiv -U_V(S, V, N)$ is the pressure, and $\mu(S, V, N) \equiv U_N(S, V, N)$ is the chemical potential.

It is useful to recall that, given a function $y = Y(x, \alpha)$ with $Y_x(x, \alpha) \neq 0$, the variable x can be expressed, on fairly general grounds, in terms of y as $x = X(y, \alpha)$, with

$$X_y(y, \alpha) = \frac{1}{Y_x(X(y, \alpha), \alpha)} \qquad \text{and} \qquad X_\alpha(y, \alpha) = -\frac{Y_\alpha(X(y, \alpha), \alpha)}{Y_x(X(y, \alpha), \alpha)}. \tag{3}$$

Then, the partial derivatives of S can be identified as:

$$\begin{aligned} S_U(U, V, N) &= \frac{1}{T(S(U, V, N), V, N)} \equiv \left(\frac{1}{T}\right)(U, V, N); \\ S_V(U, V, N) &= \frac{P(S(U, V, N), V, N)}{T(S(U, V, N), V, N)} \equiv \left(\frac{P}{T}\right)(U, V, N); \\ S_N(U, V, N) &= -\frac{\mu(S(U, V, N), V, N)}{T(S(U, V, N), V, N)} \equiv -\left(\frac{\mu}{T}\right)(U, V, N). \end{aligned} \tag{4}$$

It is now possible to show that the maximum principle, along with the extensivity and additivity properties, underlies the concavity of the entropy function. Let λ be any number with $0 < \lambda < 1$. Furthermore, let (U_1, V_1, N_1) and (U_2, V_2, N_2) identify two generic macroscopic states of the system.

Imagine, then, to form a single isolated system by putting together a fraction $1-\lambda$ of (U_1, V_1, N_1) and a fraction λ of (U_2, V_2, N_2). Once the exchange of U, V, and N between the two subsystems is allowed, the overall system evolves until its entropy reaches a value $S((1-\lambda)\, U_1 + \lambda U_2,...)$ which is larger than (or at most equal to) the initial value $S((1-\lambda)\, U_1,...) + S(\lambda U_2,...)$. Thanks to the extensivity of the entropy, this readily implies that S is a *concave* function of U, V, and N:

$$S((1-\lambda)\, U_1 + \lambda U_2,...) \geqslant (1-\lambda)\, S(U_1, V_1, N_1) + \lambda S(U_2, V_2, N_2). \tag{5}$$

In deriving Eq. (5), we have tacitly assumed that the state space is a convex set. This assumption is physically reasonable as, for instance, the set $U > U_0$, $V > 0$, and $N > 0$ is an open convex subset of $\mathscr{R}^3$.(2)

As is well known, the occurrence of an equality sign in (5) is linked with the phenomenon of phase coexistence, i.e., with the occurrence of a first-order phase transition. In such a case, the system is macroscopically inhomogeneous and the state $((1-\lambda)\, U_1 + \lambda U_2,...)$ is interpreted as a mixture of the phases (U_1, V_1, N_1) and (U_2, V_2, N_2). Hence, unless two distinct thermodynamic phases can coexist, $S(U, V, N)$ is a *strictly* concave function of U, V, N (i.e., Eq. (5) holds as a strict inequality).

Owing to the concavity of the entropy, the Hessian form of S is negative semidefinite (see Theorem 3 in Appendix A of ref. 2), a property that is usually expressed as $\mathrm{d}^2 S \leqslant 0$. Upon taking in Eq. (5) $N_1 = N_2$, the (U, V) Hessian of S turns out to be negative semidefinite as well. This condition yields the inequalities:(3)

$$S_{UU} \leqslant 0, \quad S_{VV} \leqslant 0, \qquad \text{and} \qquad S_{UU} S_{VV} - S_{UV}^2 \geqslant 0, \tag{6}$$

which are to be satisfied for all (U, V, N). These inequalities represent the conditions of thermodynamic stability for a system at equilibrium. It follows from Eqs. (6) that the constant-volume and constant-pressure heat capacities and the isothermal and isentropic compressibilities are non negative quantities.(1) Similar stability conditions do also hold for $U(S, V, N)$. In fact, a rather straightforward calculation along the same lines as those leading to Eqs. (B33)–(B35) of ref. 2, yields:

$$\begin{aligned}
U_{SS}(S, V, N) &= T_S(S, V, N) = -T(S, V, N)^3\, S_{UU}(U(S, V, N), V, N) \geqslant 0;\\
U_{VV}(S, V, N) &= -P_V(S, V, N) = -T(S, V, N)\\
&\qquad \times [S_{VV}(U(S, V, N), V, N) - 2S_{UV}(U(S, V, N), V, N)\\
&\qquad \cdot P(S, V, N) + S_{UU}(U(S, V, N), V, N) \cdot P(S, V, N)^2] \geqslant 0;\\
U_{SS} U_{VV} - U_{SV}^2 &= T(S, V, N)^4\, (S_{UU} S_{VV} - S_{UV}^2) \geqslant 0.
\end{aligned} \tag{7}$$

As for the sign of U_{VV}, note that the quantity within square brackets is the value taken in $(1, -P(S, V, N))$ by the (U, V) Hessian of S relative to $(U(S, V, N), V, N)$.

Now, let us consider an isolated system composed of two weakly interacting subsystems (say, 1 and 2), not necessarily made of the same substance, which, after removing an internal wall, may exchange energy and one more extensive quantity (e.g., the volume V) between each other. Hereafter, we shall omit in the notation explicit reference to any other extensive parameter that is separately conserved for each subsystem. The equilibrium state eventually reached by the system is the state that maximizes the total entropy

$$\tilde{S}(U_1, V_1; U, V) = S^{(1)}(U_1, V_1) + S^{(2)}(U - U_1, V - V_1) \tag{8}$$

with respect to the parameters of subsystem 1. In Eq. (8), U and V are the (fixed) values of energy and volume pertaining to the entire system. It is worth noting that the concavity of $S^{(1)}$ and $S^{(2)}$ implies that $\tilde{S}$ as well is a concave function of U_1 and V_1:

$$\begin{aligned}
&\tilde{S}((1-\lambda)\, U_1^{(A)} + \lambda U_1^{(B)}, (1-\lambda)\, V_1^{(A)} + \lambda V_1^{(B)}; U, V) \\
&\quad = S^{(1)}((1-\lambda)\, U_1^{(A)} + \lambda U_1^{(B)}, \ldots) + S^{(2)}(U - (1-\lambda)\, U_1^{(A)} - \lambda U_1^{(B)}, \ldots) \\
&\quad = S^{(1)}((1-\lambda)\, U_1^{(A)} + \lambda U_1^{(B)}, \ldots) + S^{(2)}((1-\lambda)(U - U_1^{(A)}) + \lambda (U - U_1^{(B)}), \ldots) \\
&\quad \geqslant (1-\lambda)\, \tilde{S}(U_1^{(A)}, V_1^{(A)}; U, V) + \lambda \tilde{S}(U_1^{(B)}, V_1^{(B)}; U, V).
\end{aligned} \tag{9}$$

As a result, the (U_1, V_1) Hessian of $\tilde{S}$ is negative semidefinite, which implies:

$$\tilde{S}_{U_1U_1} \leqslant 0, \quad \tilde{S}_{V_1V_1} \leqslant 0, \qquad \text{and} \qquad \tilde{S}_{U_1U_1}\tilde{S}_{V_1V_1} - \tilde{S}^2_{U_1V_1} \geqslant 0. \tag{10}$$

We now turn to the maximum condition for $\tilde{S}$. The necessary conditions for any extremal point (U_1^0, V_1^0) of $\tilde{S}$ are:

$$\tilde{S}_{U_1} = 0 \Rightarrow \left(\frac{1}{T}\right)^{(1)} (U_1^0, V_1^0) = \left(\frac{1}{T}\right)^{(2)} (U - U_1^0, V - V_1^0); \tag{11}$$

$$\tilde{S}_{V_1} = 0 \Rightarrow \left(\frac{P}{T}\right)^{(1)} (U_1^0, V_1^0) = \left(\frac{P}{T}\right)^{(2)} (U - U_1^0, V - V_1^0). \tag{12}$$

These equations merely express the well known fact that the conditions of thermal and mechanical equilibrium between subsystems 1 and 2 entail the same values of temperature and pressure for both subsystems. Furthermore, because of the concavity property, any extremum of $\tilde{S}$ is necessarily a global maximum, which is moreover strict if $\tilde{S}$ is strictly concave (see Theorem 1 and the corollary of Theorem 2 in Appendix A of ref. 2).

The solution to Eqs. (11) and (12) is generally unique (say, $U_1^0(U,V)$ and $V_1^0(U,V)$). In fact, even if the final equilibrium state hosted two coexisting phases, the values of energy and volume of each subsystem would be uniquely determined from (11) and (12), owing to the fact that N_1 and N_2 are fixed. Note that the *derivatives* of

$$\mathscr{S}(U,V) \equiv \tilde{S}(U_1^0(U,V), V_1^0(U,V); U, V) \tag{13}$$

are well-defined only when the point of maximum of $\tilde{S}$ is unique. In this case:

$$\begin{aligned}
\mathscr{S}_U &= \tilde{S}_{U_1} \cdot (U_1^0)_U + \tilde{S}_{V_1} \cdot (V_1^0)_U + \tilde{S}_U = \tilde{S}_U \\
&= \left(\frac{1}{T}\right)^{(2)} (U - U_1^0(U,V), V - V_1^0(U,V)) \equiv \left(\frac{1}{T}\right)(U,V) > 0; \\
\mathscr{S}_V &= \tilde{S}_{U_1} \cdot (U_1^0)_V + \tilde{S}_{V_1} \cdot (V_1^0)_V + \tilde{S}_V = \tilde{S}_V \\
&= \left(\frac{P}{T}\right)^{(2)} (U - U_1^0(U,V), V - V_1^0(U,V)) \equiv \left(\frac{P}{T}\right)(U,V).
\end{aligned} \tag{14}$$

We further notice that, if $S^{(1)}$ and $S^{(2)}$ happen to be the same function S (i.e., they pertain to the same substance), then $\mathscr{S}(U,V) = S(U,V,N_1+N_2)$ is a concave function of U and V.

We now proceed to demonstrate that the maximum entropy principle can be reformulated as a minimum principle for the total energy, under a constraint on the value of the total entropy. To begin with, we call $U^{(1)}(S_1, V_1)$ the energy function of subsystem 1, obtained from $S_1 = S^{(1)}(U_1, V_1)$ by solving the latter with respect to U_1. Similarly, let $U^{(2)}(S_2, V_2)$ be the energy of subsystem 2. The crucial step in our proof of the minimum energy principle will be to show that $U^{(1)}$ and $U^{(2)}$ are convex functions. To this aim, all we need to recall is that $U^{(1)}(S,V)$ (as well as $U^{(2)}$) is an increasing function of its former argument, since $U_S^{(1)}(S,V) = T^{(1)}(S,V) > 0$. Setting $S_A = S^{(1)}(U_A, V_A)$ and $S_B = S^{(1)}(U_B, V_B)$, the concavity of $S^{(1)}$,

$$\begin{aligned}
&S^{(1)}((1-\lambda)\, U_A + \lambda U_B, (1-\lambda)\, V_A + \lambda V_B) \\
&\qquad \geqslant (1-\lambda)\, S^{(1)}(U_A, V_A) + \lambda S^{(1)}(U_B, V_B),
\end{aligned} \tag{15}$$

can be rewritten as

$$(1-\lambda)\,S_A+\lambda S_B \leqslant S^{(1)}((1-\lambda)\,U^{(1)}(S_A,V_A)+\lambda U^{(1)}(S_B,V_B),\,(1-\lambda)\,V_A+\lambda V_B). \tag{16}$$

After evaluating $U^{(1)}$ at the point $((1-\lambda)\,S_A+\lambda S_B,\,(1-\lambda)\,V_A+\lambda V_B)$, it immediately follows from Eq. (16) that:

$$\begin{aligned}&U^{(1)}((1-\lambda)\,S_A+\lambda S_B,\,(1-\lambda)\,V_A+\lambda V_B)\\&\qquad\leqslant(1-\lambda)\,U^{(1)}(S_A,V_A)+\lambda U^{(1)}(S_B,V_B).\end{aligned} \tag{17}$$

Under such premises, we shall now prove that, if the total entropy takes the value $S\equiv\mathscr{S}(U,V)$, then the function

$$\tilde{U}(S_1,V_1;S,V)=U^{(1)}(S_1,V_1)+U^{(2)}(S-S_1,V-V_1), \tag{18}$$

attains its minimum for $V_1=V_1^0(U,V)$ and $S_1=S^{(1)}(U_1^0(U,V),V_1^0(U,V))\equiv S_1^0(U,V)$, where $(U_1^0(U,V),V_1^0(U,V))$ is *any* solution to Eqs. (11) and (12). Moreover, the minimum value of $\tilde{U}$ is U.

We start noting, using an argument identical to that already developed for $\tilde{S}$, that $\tilde{U}$ is a convex function of S_1 and V_1. Therefore, in order to achieve our goal, all we need to show is that the first-order derivatives of $\tilde{U}$ at $(S_1^0(U,V),V_1^0(U,V))$ are both zero, since then the convexity of $\tilde{U}$ allows one to conclude that the extremum is a global minimum.

The general expression of the first-order derivatives of $\tilde{U}$ is:

$$\begin{aligned}\tilde{U}_{S_1}&=T^{(1)}(S_1,V_1)-T^{(2)}(S-S_1,V-V_1)\\&=S_{U_1}^{(1)}(U^{(1)}(S_1,V_1),V_1)^{-1}-S_{U_2}^{(2)}(U^{(2)}(S-S_1,V-V_1),V-V_1)^{-1}\\&\propto\left(\frac{1}{T}\right)^{(2)}(U^{(2)}(S-S_1,V-V_1),V-V_1)-\left(\frac{1}{T}\right)^{(1)}(U^{(1)}(S_1,V_1),V_1);\end{aligned} \tag{19}$$

$$\begin{aligned}\tilde{U}_{V_1}&=-P^{(1)}(S_1,V_1)+P^{(2)}(S-S_1,V-V_1)\\&=\left(\frac{P}{T}\right)^{(2)}(U^{(2)}(S-S_1,V-V_1),V-V_1)\cdot T^{(2)}(S-S_1,V-V_1)\\&\quad-\left(\frac{P}{T}\right)^{(1)}(U^{(1)}(S_1,V_1),V_1)\cdot T^{(1)}(S_1,V_1).\end{aligned} \tag{20}$$

When $S_1 = S_1^0(U,V)$ and $V_1 = V_1^0(U,V)$, the energy of subsystem 1 is

$$U^{(1)}(S_1^0(U,V), V_1^0(U,V)) = U_1^0(U,V), \tag{21}$$

since $U^{(1)}$ is the inverse of $S^{(1)}$. Moreover,

$$\begin{aligned} S^{(2)}(U - U_1^0(U,V), V - V_1^0(U,V)) &= \mathscr{S}(U,V) - S^{(1)}(U_1^0(U,V), V_1^0(U,V)) \\ &= S - S_1^0(U,V), \end{aligned} \tag{22}$$

which implies:

$$U^{(2)}(S - S_1^0(U,V), V - V_1^0(U,V)) = U - U_1^0(U,V). \tag{23}$$

Given Eqs. (21) and (23), it follows from Eq. (11) that $\tilde{U}_{S_1} = 0$. This result, when combined with Eq. (12), yields $\tilde{U}_{V_1} = 0$. Finally, the absolute minimum of $\tilde{U}$ is clearly U (see Eqs. (21) and (23)) and this completes our proof. We further note that $\mathscr{U}(S,V) = \min_{S_1,V_1} \tilde{U}(S_1, V_1; S, V)$ is the inverse function of $\mathscr{S}(U,V)$. In fact, for arbitrary U and V, we have shown that $\mathscr{U}(\mathscr{S}(U,V), V) = U$. We point out that the hypothesis according to which the subsystems can only exchange two extensive parameters between each other does not affect the generality of our proof of the minimum energy principle; rather, this restriction simply avoids the use of a cumbersome notation.

A different derivation of the minimum energy principle, which does not resort to the convexity of $\tilde{U}$, is also viable. In this case, one must show that the (S_1, V_1) Hessian of $\tilde{U}$ for $V_1 = V_1^0(U,V)$ and $S_1 = S_1^0(U,V)$ is positive definite. Actually, what can be achieved this way is a weaker result, i.e., that the Hessian of $\tilde{U}$ at the extremal point is positive *semi*definite.

Using Eqs. (7), one immediately gets for $V_1 = V_1^0(U,V)$ and $S_1 = S_1^0(U,V)$:

$$\begin{aligned} \tilde{U}_{S_1S_1} &= -T^0(U,V)^3\, \tilde{S}_{U_1U_1} \geqslant 0; \\ \tilde{U}_{V_1V_1} &= -T^0(U,V)(\tilde{S}_{V_1V_1} - 2\tilde{S}_{U_1V_1} P^0(U,V) + \tilde{S}_{U_1U_1} P^0(U,V)^2) \geqslant 0; \\ \tilde{U}_{S_1V_1} &= -T^0(U,V)^2\,(-\tilde{S}_{U_1U_1} P^0(U,V) + \tilde{S}_{U_1V_1}), \end{aligned} \tag{24}$$

where $T^0(U,V) = T^{(1)}(S_1^0(U,V), V_1^0(U,V))$, $P^0(U,V) = P^{(1)}(S_1^0(U,V), V_1^0(U,V))$, whereas the arguments of the second-order $\tilde{S}$ derivatives are $U_1^0(U,V), V_1^0(U,V), U$, and V. Equations (24) also lead to:

$$\tilde{U}_{S_1S_1}\tilde{U}_{V_1V_1} - \tilde{U}^2_{S_1V_1} = T^0(U,V)^4\,(\tilde{S}_{U_1U_1}\tilde{S}_{V_1V_1} - \tilde{S}^2_{U_1V_1}) \geqslant 0, \tag{25}$$

which concludes the proof that the Hessian of $\tilde{U}$ is positive semidefinite in the final equilibrium state. Besides the general impossibility to conclude, on account of the above inequalities, that the $\tilde{U}$ extremum is a minimum (in fact, we are abstaining from using the convexity of $\tilde{U}$), the intrinsic limitation of the latter proof of the minimum energy principle lies in the fact that it only applies when the subsystems are allowed to mutually exchange at most *two* extensive parameters. In fact, only in this case the character of the Hessian of $\tilde{U}$ in the final equilibrium state can be decided in a relatively simple way on the basis of the sign of the second-order derivatives.

3. MINIMUM PRINCIPLES FOR OTHER THERMODYNAMIC POTENTIALS

Thermodynamic representations other than the entropy or the energy schemes arise when describing the equilibrium of a system that is in contact with a reservoir. Let us consider, for instance, an energy reservoir (heat bath). By definition, the temperature of a heat bath is the same in any state, i.e.,

$$(S_r)_{U_r}(U_r, V_r) = \frac{1}{T}, \tag{26}$$

a constant number which does not depend on the energy U_r or the volume V_r of the reservoir. Hence, the entropy of a heat bath reads as

$$S_r(U_r, V_r) = \frac{U_r}{T} + f(V_r), \tag{27}$$

where f is an unspecified, concave function of V_r. As usual, we omitted to specify the particle number in the notation.

When a system with an entropy function $S(U, V)$ is brought into contact with a heat bath, the joint system being isolated from the outside environment, the final equilibrium state maximizes the total entropy

$$\tilde{S}(U; U_{\text{tot}}, V, V_r) = S(U, V) + S_r(U_{\text{tot}} - U, V_r), \tag{28}$$

for fixed $U_{\text{tot}} = U + U_r$, V, and V_r (we assume that a rigid and impermeable wall keeps the system separate from the bath). The maximum condition then reads:

$$\tilde{S}_U = 0 \;\Rightarrow\; S_U(U, V) = \frac{1}{T}, \tag{29}$$

which is equivalent to $U_S(S,V)=T$, $U(S,V)$ being the inverse function of $S(U,V)$. It might happen that the solution U^0 to Eq. (29) is not unique. However, if $S(U,V)$ is strictly concave, there is a unique point of maximum $U^0(T,V)$ for $\tilde{S}$, which represents the equilibrium value of the system energy. In this case, the system entropy in the joint equilibrium state is also well-defined, being $S(U^0(T,V),V)\equiv S^0(T,V)$ and $U(S^0(T,V),V)=U^0(T,V)$.

Let us now introduce the convex function of U and V given by

$$\tilde{F}(U;T,V)=U-TS(U,V). \tag{30}$$

By simply looking at its derivatives,

$$\tilde{F}_U=1-TS_U \qquad \text{and} \qquad \tilde{F}_{UU}=-TS_{UU}, \tag{31}$$

it is immediately apparent that the maximum condition for $\tilde{S}$ is also the minimum condition for $\tilde{F}$. We call $\tilde{F}$ a generalized thermodynamic potential.[4] The minimum value $F(T,V)$ of $\tilde{F}$ is the usual Helmholtz free energy. In fact, $F(T,V)$ is the Legendre transform of $U(S,V)$ with respect to S:

$$\begin{aligned} F(T,V)&=U^0(T,V)-TS(U^0(T,V),V)=U(S^0(T,V),V)-TS^0(T,V)\\ &=[U(S,V)-TS]_{S=S^0(T,V)}, \end{aligned} \tag{32}$$

where we observe that $S^0(T,V)$ is the unique solution to $U_S(S,V)=T$ (a more general case is treated below). It is rather simple to calculate the first-order F derivatives:

$$\begin{aligned} F_T&=U_T^0(T,V)-S(U^0(T,V),V)-TS_U(U^0(T,V),V)\cdot U_T^0(T,V)\\ &=-S(U^0(T,V),V)=-S^0(T,V); \end{aligned} \tag{33}$$

$$\begin{aligned} F_V&=U_V^0(T,V)-T[S_U(U^0(T,V),V)\cdot U_V^0(T,V)+S_V(U^0(T,V),V)]\\ &=-TS_V(U^0(T,V),V)=-\frac{S_V(U^0(T,V),V)}{S_U(U^0(T,V),V)}=U_V(S^0(T,V),V)\\ &=-P(S^0(T,V),V)\equiv -P^0(T,V). \end{aligned} \tag{34}$$

In order to calculate the second-order derivatives of F we make use of Eqs. (B5) and (B7) of ref. 2:

$$\begin{aligned} F_{TT}&=-S_T^0(T,V)=-\frac{1}{U_{SS}(S^0(T,V),V)}<0;\\ F_{VV}&=-P_V^0(T,V)=\frac{U_{SS}U_{VV}-U_{SV}^2}{U_{SS}(S^0(T,V),V)}\geqslant 0. \end{aligned} \tag{35}$$

It thus follows that F is a concave function of T and a convex function of V.

Let us now consider the case of multiple solutions to Eq. (29). For instance, it may happen for a particular value T_c of T that Eq. (29) is solved by all $U \in [U_A^0, U_B^0]$, with $U_A^0 = U(S_A^0, V)$ and $U_B^0 = U(S_B^0, V)$. This occurs if, between U_A^0 and U_B^0, $S(U, V)$ is a linear function of U (first-order transition at temperature T_c). In this case, $U_S(S, V) = T_c$ is satisfied for all $S \in [S_A^0, S_B^0]$, and U_S cannot be inverted as a function of S. However, the function $\tilde{F}$ is still well-defined, along with its global minimum $F(T_c, V)$. Furthermore, Eq. (32) still holds, provided we call $S^0(T, V)$ the *unique* solution to $U(S, V) = U^0(T, V)$. In particular,

$$\lim_{T \to T_C^-} F(T, V) = U_A^0 - T_c S_A^0 = U_B^0 - T_c S_B^0 = \lim_{T \to T_C^+} F(T, V), \tag{36}$$

which means that $F(T, V)$ is continuous for $T = T_c$. However, $F(T, V)$ has a cusp-like singularity for $T = T_c$:

$$\lim_{T \to T_C^-} F_T(T, V) = -S_A^0 \neq -S_B^0 = \lim_{T \to T_C^+} F_T(T, V). \tag{37}$$

As a further example, let us consider the case of a system exchanging energy and volume with a reservoir. The values of temperature and pressure are both fixed for the reservoir:

$$(S_r)_{U_r}(U_r, V_r) = \frac{1}{T} \qquad \text{and} \qquad (S_r)_{V_r}(U_r, V_r) = \frac{P}{T}. \tag{38}$$

Therefore, the bath entropy is now fully specified as

$$S_r(U_r, V_r) = \frac{U_r + PV_r}{T}. \tag{39}$$

The maximum conditions for the total entropy

$$\tilde{S}(U, V; U_{\text{tot}}, V_{\text{tot}}) = S(U, V) + S_r(U_{\text{tot}} - U, V_{\text{tot}} - V) \tag{40}$$

then read:

$$\tilde{S}_U = 0 \;\Rightarrow\; S_U(U, V) = \frac{1}{T}; \tag{41}$$

$$\tilde{S}_V = 0 \;\Rightarrow\; S_V(U, V) = \frac{P}{T}. \tag{42}$$

Assuming a unique solution for the above equations, one finds $U = U^0(T, P)$ and $V = V^0(T, P)$. Upon assuming $S^0(T, P)$ to be $S(U^0(T, P),$

$V^0(T,P))$, one has $U(S^0(T,P), V^0(T,P)) = U^0(T,P)$. Moreover, Eqs. (41) and (42) are equivalent to $U_S(S,V) = T$ and $U_V(S,V) = -P$.

As we did previously for a system in contact with a heat bath, it is appropriate to introduce the auxiliary, convex function of U and V, given by

$$\tilde{G}(U,V;T,P) = U - TS(U,V) + PV. \tag{43}$$

Clearly, $\tilde{G}$ attains its minimum for $U = U^0(T,P)$ and $V = V^0(T,P)$, since

$$\tilde{G}_U = 1 - TS_U \qquad \text{and} \qquad \tilde{G}_V = -TS_V + P \tag{44}$$

are both zero. The minimum value $G(T,P)$ of $\tilde{G}$ is the Gibbs free energy. In fact,

$$\begin{aligned} G(T,P) &= U^0(T,P) - TS(U^0(T,P), V^0(T,P)) + PV^0(T,P) \\ &= U(S^0(T,P), V^0(T,P)) - TS^0(T,P) + PV^0(T,P) \\ &= [U(S,V) - TS + PV]_{S=S^0(T,P),\, V=V^0(T,P)} \end{aligned} \tag{45}$$

is the Legendre transform of $U(S,V)$ with respect to S and V, which have been replaced by their conjugate variables T and $-P$ (observe that $(S^0(T,P), V^0(T,P))$ is, by our previous assumption, the unique solution to $U_S(S,V) = T$ and $U_V(S,V) = -P$). The first-order derivatives of G are simply calculated as:

$$\begin{aligned} G_T &= U_T^0(T,P) - S^0(T,P) - T[S_U(U^0(T,P), V^0(T,P)) \cdot U_T^0(T,P) \\ &\qquad + S_V(U^0(T,P), V^0(T,P)) \cdot V_T^0(T,P)] + PV_T^0(T,P) \\ &= -S^0(T,P); \end{aligned} \tag{46}$$

$$\begin{aligned} G_P &= U_P^0(T,P) - T[S_U(U^0(T,P), V^0(T,P)) \cdot U_P^0(T,P) \\ &\qquad + S_V(U^0(T,P), V^0(T,P)) \cdot V_P^0(T,P)] + V^0(T,P) + PV_P^0(T,P) \\ &= V^0(T,P), \end{aligned} \tag{47}$$

whereas, with the help of Eqs. (B20)–(B22) and (B24) of ref. 2, the second-order G derivatives turn out to be:

$$\begin{aligned} G_{TT} &= -S_T^0(T,P) = -\frac{U_{VV}(S^0(T,P), V^0(T,P))}{U_{SS}U_{VV} - U_{SV}^2} \leqslant 0; \\ G_{PP} &= V_P^0(T,P) = -\frac{U_{SS}(S^0(T,P), V^0(T,P))}{U_{SS}U_{VV} - U_{SV}^2} \leqslant 0; \\ G_{TT}G_{PP} - G_{TP}^2 &= (U_{SS}U_{VV} - U_{SV}^2)^{-1} > 0. \end{aligned} \tag{48}$$

Hence, G is a concave function of both T and P.

Summing up, when a system is in thermal and mechanical contact with a reservoir, it is $\tilde{G}$ (the generalized Gibbs potential) that is minimum at equilibrium, not the Gibbs free energy as is sometimes stated. Similarly, if the wall between the system and the reservoir is permeable to the flow of energy and particles while being restrictive to volume, it is $\tilde{A}(U, N; T, V, \mu) = U - TS(U, V, N) - \mu N$ that is minimized at equilibrium, its minimum value being the system grand potential.

Needless to say, equivalent maximum principles hold for the functions $S(U, V) - (1/T)\, U$ and $S(U, V) - (1/T)\, U - (P/T)\, V$, equal to $-(1/T)\, \tilde{F}(U; T, V)$ and $-(1/T)\, \tilde{G}(U, V; T, P)$, respectively. Their maximum loci correspond to the usual Massieu functions.

It is worth observing that the minimization of the generalized Gibbs potential is correct also in the common situation of determining the equilibrium between two systems that are in contact with the same energy and volume reservoir. In fact, the maximum condition for the total entropy

$$\tilde{S} = S^{(1)}(U_1, V_1) + S^{(2)}(U_2, V_2) + \frac{U_{\text{tot}} - U_1 - U_2 + P(V_{\text{tot}} - V_1 - V_2)}{T} \tag{49}$$

can be rather obviously translated into the minimum condition for the convex function

$$\begin{aligned} \tilde{G}(U_1, V_1, U_2, V_2; T, P) &= \tilde{G}^{(1)}(U_1, V_1; T, P) + \tilde{G}^{(2)}(U_2, V_2; T, P) \\ &= U_1 - TS^{(1)}(U_1, V_1) + PV_1 + U_2 - TS^{(2)}(U_2, V_2) + PV_2, \end{aligned} \tag{50}$$

as immediately follows from computing the partial derivatives of Eq. (50).

In closing, we re-examine the question of the shape of the thermodynamic potentials for a system undergoing a discontinuous phase transition. The Gibbs free energy is the thermodynamic potential that is usually considered for describing the phases of matter. This quantity stems from $\tilde{G}$ after tracing the locus of its global minimum as a function of T and P. When a discontinuous phase transition line is approached, a piece of ruled surface appears in the profile of the fundamental relation, and then also in the graph of $\tilde{G}$, which remains convex, even though not everywhere strictly convex. This implies a discontinuous evolution for the location of the absolute $\tilde{G}$ minimum (not for the absolute minimum itself!), i.e., a jump from one valley to another as soon as the coexistence line is crossed.

While one single minimum is the rule for $\tilde{G}$ in the thermodynamic limit, this is not generally true for a *finite* system. In the framework of the statistical-mechanical foundations of thermodynamics, this means that the microcanonical $S(U, V, N)$ of the finite system may not be everywhere concave.[(5)] In fact, near the would-be first-order transition point, a dip will usually appear in the S profile which is responsible for the phenomenon of metastability. In turn, $\tilde{G}$ is not everywhere convex and a competition arises between two different local minima: while the deepest minimum characterizes the most stable phase, the other one, as long as it is present, will be the sign that another phase is at least metastable (this is the usual occurrence in mean-field treatments of first-order transitions).

The infinite-size behavior of $\tilde{G}$ is sketched in Fig. 1, where its typical profile close to a first-order transition point is shown. Here, $\tilde{G}(U, V; T, P)$ is plotted as a function of V/N at constant T, for a number of values of P across the coexistence line relative to, say, the liquid and the vapor of a substance (only a slice of the Gibbs surface along a locus $U(V)$ passing through the actual point of minimum of $\tilde{G}$ is represented in the figure). The abscissa of the $\tilde{G}$ minimum gives the specific volume of the most stable system phase for the given T and P values. At the same time, the G profile will show, both as a function of P at constant T as well as a function of T at constant P, a cusp-like singularity of the same kind discussed before for the Helmholtz free energy, which is responsible for the discontinuities of volume and entropy, respectively, across the transition.

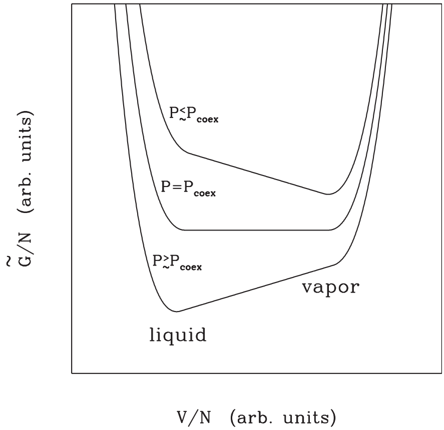

Fig. 1. The figure shows how the profile of $\tilde{G}$ plotted as a function of the volume V is modified when approaching a first-order phase transition, like that from vapor to liquid. As the pressure changes—at constant temperature—across the coexistence value P_{coex}, one observes a thermodynamic-stability crossover from the vapor to the liquid phase (see text). Note that, with the single exception of $P = P_{\mathrm{coex}}$, the point of minimum of $\tilde{G}$ is regular (in particular, the tangent plane is well-defined there).

4. CONCLUSIONS

Starting from the maximum entropy principle, we have provided a detailed derivation of the principle of minimum energy and of similar principles for thermodynamic potentials and Massieu functions, by resorting to the mathematical theory of concave many-variable functions. This calculation was also motivated by the fact that standard reference books on thermodynamics usually do not give enough information about this point. In our opinion, proving the interchangeability of all thermodynamic representations is a necessary prerequisite that allows the interested reader to fully appreciate the elegance of the thermodynamic formalism.

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REFERENCES

1. H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, 1985).
2. An expanded version of the present article, containing two appendices with some useful technical material, is available at http://www.me.infm.it/~prestip. In particular, Appendix A of the web version summarizes some properties of concave (and convex) functions that are used in the following, while Appendix B collects a number of relevant results concerning Legendre transforms and their derivatives.
3. Observe that for a generic quadratic form of two variables, $H(\xi_1, \xi_2) = A\xi_1^2 + 2B\xi_1\xi_2 + C\xi_2^2 = A[(\xi_1 + (B/A)\,\xi_2)^2 + (\xi_2^2/A^2) \times (AC - B^2)]$ (where $A \neq 0$), H is positive definite iff $A > 0$ and $AC - B^2 > 0$, and negative definite iff $A < 0$ and $AC - B^2 > 0$.
4. Alternatively, one can define $\tilde{F}$ as $U(S, V) - TS$. In this case, $\tilde{F}$ would be a function of S which parametrically depends on T and V. Anyway, the minimum and the convexity properties of $\tilde{F}$ remain the same (see Appendix B of ref. 2).
5. See, for instance, I. Ispolatov and E. G. D. Cohen, On first-order phase transitions in microcanonical and canonical non-extensive systems, *Physica A* **295**:475–487 (2001).