

ON SUBADDITIVITY AND CONVEXITY PROPERTIES OF THERMODYNAMIC FUNCTIONS†

L. GALGANI

Istituto di Fisica dell'Università, Milan, Italy

AND

A. SCOTTI

*C.C.R. Euratom, Ispra, Italy and Istituto di Fisica dell'Università,
Milan, Italy*

ABSTRACT

It is pointed out that the usual basic postulate of increase of entropy for an isolated system, as stated for example by Tisza and Callen, if mathematically formalized, is expressed as a superadditivity property of entropy. This fact has two kinds of implications: (a) it allows one to deduce in a very direct and mathematically clear way stability properties such as $C_V \geq 0$ and $K_T \geq 0$ and the equivalence of various thermodynamic schemes as expressed for example by the fact that the 'minimum' property of the free energy is a consequence of the 'maximum' property of entropy; (b) it makes it possible to establish a link with foundations research, notably the system developed by Giles, where superadditivity of entropy appears as a consequence of other axioms.

INTRODUCTION

Recent developments in the foundations of thermodynamics are of two kinds. On the one hand¹⁻⁴ one can find attempts to make rigorous the connection between the possibility of defining entropy and the classical statements of the second principle. On the other hand⁵⁻⁶ the concept of entropy is taken for granted and some of its properties are assumed in an axiomatic way, so that attention is turned to deducing rigorous consequences therefrom: these works are on the line of Gibbs.

In statistical thermodynamics both attitudes have their counterpart. The second approach has been intensively investigated particularly since 1963, when Ruelle^{7,8} was able to study in a rigorous way the problem of the so-called 'thermodynamic limit' on the basis of the conditions of stability and strong tempering on the intermolecular potentials. In the technical treatment of the problem the mathematical property of superadditivity was considered and the limit thermodynamic functions turned out to have convexity properties⁹⁻¹⁴. This was just the clue to some improvements in

† Work supported in part by CNR (Consiglio Nazionale delle Ricerche).

thermodynamics itself, by the realization that superadditivity has a deep physical meaning: it expresses formally the basic postulate assumed by Tisza and Callen¹⁵. This simple property allows one to derive in a very direct way properties such as continuity and differentiability (almost everywhere) of entropy, stability conditions, extremum properties of thermodynamic potentials and Massieu functions, which had been postulated independently or derived in a more complicated or obscure way by those authors.

The way this is done is presented in the first three sections. In section 4 the physical meaning of convexity properties is illustrated and the conclusions are given in section 5.

1. ENTROPY SCHEME

We consider for definiteness and simplicity a system whose equilibrium states are characterized by the values of three extensive quantities: energy U , volume V and number of moles N ; its thermodynamic properties are deduced from the entropy S defined through the functional relation

$$S = \mathcal{S}(U, V, N) \quad (1)$$

The assumed properties of \mathcal{S} are those of homogeneity, strict monotonicity in U and superadditivity:

$$\mathcal{S}(\lambda U, \lambda V, \lambda N) = \lambda \mathcal{S}(U, V, N) \quad (\lambda \text{ real}) \quad (2)$$

$$\mathcal{S}(U_2, V, N) \geq \mathcal{S}(U_1, V, N) \Leftrightarrow U_2 \geq U_1 \quad (3)$$

$$\mathcal{S}(U_1 + U_2, V_1 + V_2, N_1 + N_2) \geq \mathcal{S}(U_1, V_1, N_1) + \mathcal{S}(U_2, V_2, N_2) \quad (4)$$

Equation 2, commonly employed, is a consequence of the postulate of extensivity of entropy: geometrically it means the \mathcal{S} is a ruled surface. Equation 3 is related to positivity of temperature; it will be used only for the passage to the energy scheme (§2). Equation 4 is the property of superadditivity which expresses physically the increasing property of entropy for isolated systems: for an isolated system of fixed U, V, N the state of unconstrained equilibrium has an entropy greater than all corresponding states of constrained equilibrium. The entropy of the state of constrained equilibrium is represented by the RHS of equation 4, in accordance with the postulate of extensivity. The postulate of increase of entropy, enunciated in words in this form also by Tisza and Callen, was formally exploited only in a way that required consideration of the thermodynamic space of configurations enlarged to include the extensive independent variables of the simple systems constituting the composite constrained one. As it is formalized in equation 4, it just gives a functional relation on the function $\mathcal{S}(U, V, N)$ itself. The power of this relation is shown by the following immediate consequence: by equations 4 and 2, with $\lambda = \frac{1}{2}$, one has

$$2\mathcal{S}\left(\frac{U_1 + U_2}{2}, \frac{V_1 + V_2}{2}, \frac{N_1 + N_2}{2}\right) \geq \mathcal{S}(U_1, V_1, N_1) + \mathcal{S}(U_2, V_2, N_2) \quad (5)$$

i.e. \mathcal{S} is a concave function. By known theorems on convex functions it follows that¹⁶:

- (i) $\mathcal{S}(U, V, N)$ is continuous†;
- (ii) right and left first partial derivatives of \mathcal{S} always exist; the corresponding differentiated variables are monotonically decreasing (so that they may have at most jump discontinuities in a denumerable set);
- (iii) if \mathcal{S} is twice differentiable, then one has

$$Q(x, y, z) \equiv$$

$$\frac{\partial^2 \mathcal{S}}{\partial U^2} x^2 + \frac{\partial^2 \mathcal{S}}{\partial V^2} y^2 + \frac{\partial^2 \mathcal{S}}{\partial N^2} z^2 + 2 \left\{ \frac{\partial^2 \mathcal{S}}{\partial U \partial V} xy + \frac{\partial^2 \mathcal{S}}{\partial U \partial N} xz + \frac{\partial^2 \mathcal{S}}{\partial V \partial N} yz \right\} \leq 0$$

In particular, with $\partial \mathcal{S} / \partial U = 1/T$, $\partial \mathcal{S} / \partial V = p/T$, and on the basis of (iii) one can prove the stability conditions:

$$C_V = \left(T \frac{\partial \mathcal{S}}{\partial T} \right)_V \geq 0, \quad K_T = - \frac{1}{V} \left(\frac{\partial p}{\partial V} \right)_T \geq 0 \quad (6)$$

which will, however, be derived in a more direct way in §3.

Properties (i) and (ii) are independently postulated by the quoted authors. Tisza derives the stability conditions 6 in a less direct way, while other treatments have been criticized¹⁷.

2. ENERGY SCHEME

By equation 3 it is possible to invert the functional relation 1 and obtain

$$U = \mathcal{U}(S, V, N) \quad (7)$$

where \mathcal{U} is defined by the identity in S , for any V and N ,

$$\mathcal{S}[\mathcal{U}(S, V, N), V, N] \equiv S \quad (8)$$

We then have that \mathcal{U} is convex and homogeneous,

$$\mathcal{U} \left(\frac{S_1 + S_2}{2}, \frac{V_1 + V_2}{2}, \frac{N_1 + N_2}{2} \right) \leq \frac{1}{2} \{ \mathcal{U}(S_1, V_1, N_1) + \mathcal{U}(S_2, V_2, N_2) \} \quad (9)$$

$$\mathcal{U}(\lambda S, \lambda V, \lambda N) = \lambda \mathcal{U}(S, V, N) \quad (10)$$

Equation 9 follows from equations 5 and 3, by appropriate repeated use of equation 8

$$\begin{aligned} \mathcal{S} \left[\mathcal{U} \left(\frac{S_1 + S_2}{2}, \frac{V_1 + V_2}{2}, \frac{N_1 + N_2}{2} \right), \frac{V_1 + V_2}{2}, \frac{N_1 + N_2}{2} \right] &= \frac{S_1 + S_2}{2} \\ &= \frac{1}{2} \{ \mathcal{S}[\mathcal{U}(S_1, V_1, N_1), V_1, N_1] + \mathcal{S}[\mathcal{U}(S_2, V_2, N_2), V_2, N_2] \} \\ &\leq \mathcal{S} \left(\frac{\mathcal{U}(S_1, V_1, N_1) + \mathcal{U}(S_2, V_2, N_2)}{2}, \frac{V_1 + V_2}{2}, \frac{N_1 + N_2}{2} \right) \end{aligned}$$

† Strictly speaking this is true only if the function \mathcal{S} is assumed to be measurable.

Equation 10 follows from equations 2 and 3, again using equation 8 :

$$\begin{aligned} \mathcal{S}[\mathcal{U}(\lambda S, \lambda V, \lambda N), \lambda V, \lambda N] &= \lambda S = \lambda \mathcal{S}[\mathcal{U}(S, V, N), V, N] \\ &= \mathcal{S}[\lambda \mathcal{U}(S, V, N), \lambda V, \lambda N] \end{aligned}$$

From equations 9 and 10 it now follows that \mathcal{U} is subadditive

$$\mathcal{U}(S_1 + S_2, V_1 + V_2, N_1 + N_2) \leq \mathcal{U}(S_1, V_1, N_1) + \mathcal{U}(S_2, V_2, N_2) \quad (11)$$

an inequality that can be physically interpreted in complete analogy to the case of inequality 4, as expressing the decreasing property of energy in isolated systems when internal constraints are released.

We note in passing that it would be possible to derive the subadditivity of \mathcal{U} directly from the superadditivity of \mathcal{S} , which is essentially the same procedure used by Gibbs himself, and then get the convexity through homogeneity. Indeed one has

$$\begin{aligned} \mathcal{S}[\mathcal{U}(S_1 + S_2, V_1 + V_2, N_1 + N_2), V_1 + V_2, N_1 + N_2] &= S_1 + S_2 \\ &= \mathcal{S}[\mathcal{U}(S_1, V_1, N_1), V_1, N_1] + \mathcal{S}[\mathcal{U}(S_2, V_2, N_2), V_2, N_2] \\ &\leq \mathcal{S}[\mathcal{U}(S_1, V_1, N_1) + \mathcal{U}(S_2, V_2, N_2), V_1 + V_2, N_1 + N_2] \end{aligned}$$

The first way of proceeding can be extended to Legendre transform representations.

3. LEGENDRE TRANSFORM SCHEMES

The Legendre transform $g(t)$ of a convex function $f(x)$ is given¹⁰ by

$$g(t) = \inf_x \{f(x) - tx\}, \quad \inf_x \left(\frac{\partial f}{\partial x}\right)^- < t < \sup_x \left(\frac{\partial f}{\partial x}\right)^+ \quad (12)$$

where $(\partial f/\partial x)^\pm$ is the right (left) derivative. Indeed if $f(x)$ is differentiable and strictly convex, the infimum is actually a minimum, reached at the unique point $\bar{x}(t)$ such that $\left.\frac{\partial f}{\partial x}\right|_{x=\bar{x}(t)} = t$, so that equation 12 can be reduced to

the usual definition of the Legendre transform. Definition 12 is more advantageous, however, because it makes explicit the change of variable and, in addition, because it is meaningful also for general convex functions that may have discontinuities in the derivatives and can be linear in some intervals.

Coming now for definiteness to the case of a convex function of two variables $f(x, y)$,

$$f\left(\frac{x_1 + x_2}{2}, \frac{y_1 + y_2}{2}\right) \leq \frac{1}{2}\{f(x_1, y_1) + f(x_2, y_2)\}$$

we may consider the partial Legendre transform

$$g(t, y) = \inf_x \{f(x, y) - tx\}$$

for which the following convexity properties are easily established^{18, 19}

$$g\left(\frac{t_1 + t_2}{2}, y\right) \geq \frac{1}{2}\{g(t_1, y) + g(t_2, y)\}$$

$$g\left(t, \frac{y_1 + y_2}{2}\right) \leq \frac{1}{2}\{g(t, y_1) + g(t, y_2)\}$$

i.e. Legendre transformation inverts the convexity properties in the transformed variables, while leaving unchanged those in the non-transformed variables. Indeed one has:

$$\begin{aligned} \inf_x \left\{ f(x, y) - \frac{t_1 + t_2}{2} x \right\} &= \frac{1}{2} \inf_x \{ f(x, y) - t_1 x + f(x, y) - t_2 x \} \\ &\geq \frac{1}{2} \{ \inf_x [f(x, y) - t_1 x] + \inf_x [f(x, y) - t_2 x] \} \end{aligned}$$

$$\begin{aligned} \inf_x \left\{ f\left(x, \frac{y_1 + y_2}{2}\right) - tx \right\} &\leq f\left(\frac{\bar{x}(t, y_1) + \bar{x}(t, y_2)}{2}, \frac{y_1 + y_2}{2}\right) - t \frac{\bar{x}(t, y_1) + \bar{x}(t, y_2)}{2} \\ &\leq \frac{1}{2} \{ f[\bar{x}(t, y_1), y_1] - t\bar{x}(t, y_1) + f[\bar{x}(t, y_2), y_2] - t\bar{x}(t, y_2) \} \\ &= \frac{1}{2} \{ \inf_x [f(x, y_1) - tx] + \inf_x [f(x, y_2) - tx] \} \end{aligned}$$

where

$$f[\bar{x}(y, t) - t\bar{x}(y, t)] = \inf_x \{ f(x, y) - tx \}$$

If the function $f(x, y)$ is concave, the Legendre transform is defined by analogy with equation 12 (using supremum instead of infimum) and the stated theorem on convexity properties continues to hold. So we have the general theorem concerning all possible Legendre transforms of energy (thermodynamic potentials) and entropy (Massieu functions).

Thermodynamic potentials (Massieu functions) are convex (concave) in the extensive variables and concave (convex) in the intensive ones.

From this convexity theorem, if the functions considered are assumed to be twice differentiable, stability properties now follow directly, as anticipated in § 2. Furthermore, observing that Legendre transforms are homogeneous in the extensive variables, one can derive subadditivity or superadditivity in these variables, as was done for energy in § 2. These properties too can be interpreted as expressing extremum properties with respect to states of constrained equilibrium.

4. PHYSICAL MEANING OF CONVEXITY PROPERTIES

In the same way as superadditivity of \mathcal{S} (equation 4) was considered a formalization of the postulate that the state of unconstrained equilibrium has entropy greater than all corresponding states of constrained equilibrium,

it seems quite natural to give also an analogous interpretation of the convexity property (equation 5). This interpretation is that the state of constrained equilibrium, in which the constraints are such that all component systems have equal extensive parameters, has entropy greater than all other corresponding states of constrained equilibrium.

Of course, the equivalence of these two statements comes about because of the fact that when all component systems have equal extensive variables the composite system is homogeneous, so that the LHS of equations 4 and 5 are equal. But the physical meaning of the convexity property seems much deeper and more direct than that of superadditivity. Indeed the property of convexity compares states in both of which there are constraints, and asserts that the state of maximum entropy corresponds to equipartition of extensive parameters (homogeneity). In this sense one might think this to be a natural starting point for the consideration of thermodynamics of irreversible processes, which act just in the direction of equalizing extensive parameters in every region.

Finally we remark that convexity properties in the intensive variables for Legendre transforms, which are usually not mentioned, can also be interpreted in this way, and this stands at variance with superadditivity properties, which cannot be proved in this case.

5. CONCLUSION

We have pointed out that the basic postulate of increase of entropy, as expressed by the statement that the state of unconstrained equilibrium of an isolated system has an entropy greater than all corresponding states of constrained equilibrium, if mathematically formalized, is simply expressed as a superadditivity property of entropy.

This remark has two kind of implications. First, it allows one to deduce in a very direct and mathematically clear way:

- (i) stability properties such as $C_V \geq 0$, $K_T \geq 0$, where C_V and K_T are the specific heat and the isothermal compressibility respectively;
- (ii) the equivalence of various thermodynamic schemes as expressed for example by the fact that the 'minimum' property of free energy is a consequence of the 'maximum' property of entropy.

In particular, property (i) is expressed as a concavity property of entropy and is brought to the general theorem: 'Thermodynamic potentials (Massieu functions) are convex (concave) in the extensive parameters and concave (convex) in the intensive ones'.

Secondly it is possible to establish a link between the basic postulate of the increase of entropy in the form stated above and certain more fundamental discussions of the foundations of thermodynamics, especially that of Giles³, where superadditivity of entropy for equilibrium states appears as a consequence of other axioms (Theorem 9.1.3).

REFERENCES

- ¹ H. A. Buchdahl, *Z. Phys.* **152**, 425 (1958).
- ² B. Bernstein, *J. Math. Phys.* **1**, 222 (1960).
- ³ R. Giles, *Mathematical Foundations of Thermodynamics*. Pergamon: Oxford (1964).
- ⁴ J. B. Boyling, *Comm. Math. Phys.* **10**, 52 (1968).
- ⁵ L. Tisza, *Ann. Phys.* **13**, 1 (1961).
- ⁶ H. B. Callen, *Thermodynamics*. Wiley: New York (1960).
- ⁷ D. Ruelle, *Helv. Phys. Acta*, **36**, 183 (1963).
- ⁸ D. Ruelle, *Statistical Mechanics, Rigorous Results*, W. A. Benjamin: Amsterdam (1969).
- ⁹ M. E. Fisher, *Arch. Ration. Mech. Anal.* **17**, 377 (1964).
- ¹⁰ R. B. Griffiths, *J. Math. Phys.* **6**, 1447 (1965).
- ¹¹ J. Van der Linden, *Physica*, **32**, 642 (1966).
- ¹² J. Van der Linden and P. Mazur, *Physica*, **36**, 491 (1967).
- ¹³ J. Van der Linden, *Physica*, **38**, 173 (1968).
- ¹⁴ L. Galgani, L. Manzoni and A. Scotti, *Physica*, **41**, 622 (1968).
- ¹⁵ L. Galgani and A. Scotti, *Physica*, **40**, 150 (1968).
- ¹⁶ G. H. Hardy, J. E. Littlewood and G. Pólya, *Inequalities*, Cambridge University Press: London (1959).
- ¹⁷ J. T. Lopuszanski, *Acta Physica Polonica*, **33**, 953 (1968).
- ¹⁸ S. Mandelbrojt, *C.R. Acad. Sci., Paris*, **209**, 977 (No. 11, 1939).
- ¹⁹ L. Galgani and A. Scotti, *Physica*, **42**, 242 (1969).