

Fundamental Functions in Equilibrium Thermodynamics*

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In the standard presentations of the principles of Gibbsian equilibrium thermodynamics one can find several gaps in the logic. For a subject that is as widely used as equilibrium thermodynamics, it is of interest to clear up such questions of mathematical rigor. In this paper it is shown that using convex analysis one can give a mathematically rigorous treatment of several basic aspects of equilibrium thermodynamics. On the basis of a fundamental convexity property implied by the second law, the following topics are discussed: thermodynamic stability, transformed fundamental functions (such as the Gibbs free energy), and the existence and uniqueness of possible final equilibrium states of closed composite thermodynamic systems. It is shown that a standard mathematical characterization of thermodynamic stability (involving a positive definiteness property) is sufficient but in fact not necessary for the physically superior convexity characterization of thermodynamic stability. Furthermore, it is found that functions such as the Gibbs free energy can be rigorously and globally defined using convex conjugation instead of Legendre transformation. Another result described in this paper is that equilibrium thermodynamics cannot always uniquely predict possible final equilibrium states of closed composite thermodynamic systems. © 1987 Academic Press, Inc

1. INTRODUCTION

Of the standard physical theories, classical thermodynamics is the one that has most often been criticized for the lack of rigor of the mathematics used in its presentation. In many existing mathematical investigations of thermodynamics the mathematical presentation of thermodynamics is improved by constructing a thermodynamic theory that is different from the classical presentation of thermodynamics given by Gibbs [1] (see, e.g., [2–4]). The purpose of this paper is, instead, to investigate certain mathematical aspects of equilibrium thermodynamics, leaving its Gibbsian form (as presented in, e.g., [5]) essentially unchanged.

Just as in quantum mechanics all information can in principle be obtained from wave functions, the source of all information from equilibrium thermodynamics is what Gibbs called “fundamental equations” [1] (see also [5, 6]). For example, in

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the energy representation the fundamental equation of a thermodynamic system specifies the values of the internal energy U as a function of the values of a complete set of independent extensive parameters X_1, \dots, X_n , one of which is the entropy:

$$U = U(X_1, \dots, X_n). \quad (1)$$

All equilibrium-thermodynamic information about a thermodynamic system is contained in such a fundamental equation. No set of numerical thermodynamic data of a thermodynamic system can contain more thermodynamic information about this system than is contained in its full fundamental equation. Since the fundamental equations of equilibrium thermodynamics actually specify the values of functions, and in order to make it easier to apply mathematical terminology concerning functions, they will in this paper be referred to as *fundamental functions*. For example, the function given in Eq. (1) will be referred to as a *fundamental energy function*. The existence of fundamental functions satisfying certain physically desired properties is usually postulated in equilibrium thermodynamics without completely explicit statements about their general mathematical form [5, 6]. In quantum mechanics, the situation is different: the operators representing the physical observables are assumed to be of a special mathematical form, namely, self-adjoint. This ensures, among other things, that the eigenvalues of these operators are real, so that a direct physical interpretation of these eigenvalues is possible. It would have been cumbersome to postulate instead that physical observables are represented by operators whose eigenvalues are real, without using the fact that self-adjointness is the essential mathematical property in this connection. Similarly, it would be desirable to know the general mathematical form of the main theoretical objects of equilibrium thermodynamics (i.e., fundamental functions), so that the physically desirable conclusions can be rigorously derived in a mathematical way. In other words, it is desirable to summarize the physical content of thermodynamics (including the second law) mathematically in terms of precisely stated general mathematical properties of fundamental functions.

It usually appears from textbooks on thermodynamics that not much is known about the full fundamental equation of most thermodynamic systems. According to Gibbs, "The forms of these functions, however, remains to be determined by experiment, and here we meet the greatest difficulties, and find an inexhaustible field of labor" [7]. So far there does not seem to be a systematic study of the basic aspects of equilibrium thermodynamics that is based rigorously on the general mathematical properties of fundamental functions. One of the most important mathematical properties of the fundamental function of a thermodynamic system is that for a large class of thermodynamic systems this function is convex in the energy representation. This convexity property is a consequence of the physical content of thermodynamics as expressed in, e.g., the maximum entropy principle. Convexity properties have often played an intuitive and implicit role in several parts of thermodynamics. In this paper it is shown that by giving convexity a more explicit role, the mathematical treatment of several basic aspects of equilibrium

thermodynamics can be improved. The following topics will be studied on the basis of convexity properties of fundamental energy functions: thermodynamic stability, transformed fundamental functions (such as the Gibbs free energy), and the existence and uniqueness of possible final equilibrium states of closed composite thermodynamic systems.

The mathematical investigation of convex functions, especially in connection with problems of minimization, has led to the growth of an entire new branch of mathematics: convex analysis [8]. Although convex analysis was developed more with an eye to applications in the economic sciences than in the physical sciences, it turns out to be well suited to deal with many mathematical aspects of equilibrium thermodynamics. It has been stated by Callen that "the basic problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed composite system" [5, p. 24]. This "basic problem" can generally be formulated mathematically as the problem of maximizing a concave function of several variables (the maximum entropy principle) or, analogously, as a problem of minimizing a convex function of several variables (the minimum energy principle); these are precisely the problems for which convex analysis was developed. In this paper extensive use will be made of convex analysis. The mathematical literature (in particular, [8]) should be consulted for the proofs of some results of convex analysis mentioned here. In addition, use will be made of several standard concepts and results from classical mathematical analysis [9]. Although several results described in this paper give only a formal justification for things that have been intuitively clear to thermodynamicists for a long time, there are also results that would be difficult to justify on the basis of the laws of equilibrium thermodynamics without explicitly considering the convexity of fundamental energy functions.

In Section 2 the required basic concepts and results of convex analysis are summarized briefly. In Section 3 the basic properties of fundamental energy functions are discussed. Fundamental functions are often only considered for homogeneous thermodynamic systems. Following Gibbs' first papers on thermodynamics [1], we adopt a more global view of fundamental functions: thermodynamic systems that may split up into different phases can be thermodynamically characterized by one fundamental function. The convexity of (global) fundamental energy functions will be directly related to the minimum energy principle. A natural formal definition of thermodynamic stability is given, entirely in terms of a convexity property of fundamental energy functions. This definition turns out to be not fully equivalent to the standard mathematical characterization of thermodynamic stability, which makes use of Hessians of fundamental energy functions. In terms of mathematical properties of fundamental energy functions, equilibrium states that are not thermodynamically stable can be partitioned in a natural way into multiphase states and critical points. In Section 4 some mathematical aspects of the transformation from fundamental energy functions to fundamental functions such as the Gibbs free energy are studied using convex analysis. Instead of the usual definitions of Legendre transformation as given in treatments of equilibrium thermodynamics, a

technique from convex analysis known as “convex conjugation” is shown to give a better formal definition for thermodynamic purposes. Although fundamental energy functions can be completely reconstructed from transformed fundamental functions such as the Gibbs free energy, the latter functions usually contain in a certain sense less thermodynamic information about thermodynamic systems: sets of multiphase states collapse into one point in the transformation from fundamental energy functions to other fundamental functions. All thermodynamic information contained in a fundamental energy function having as independent variables a complete set of n independent extensive parameters, is also contained in a certain n -dimensional convex set. A general thermodynamic inequality is obtained by considering convex conjugates of full fundamental energy functions. In Section 5 several applications of Gibbs’ minimum energy principle are considered using convex analysis. The existence and uniqueness of possible final equilibrium states of closed composite thermodynamic systems is discussed. A general mathematical characterization of the set of all such possible final equilibrium states is obtained. An example involving phase transitions is discussed, which shows that for closed composite thermodynamic systems the minimum energy principle may predict more than one possible final equilibrium state. In some cases final equilibrium states of composite thermodynamic systems can be found explicitly using a symmetry argument. It is shown that there are cases in which a thermodynamic system that is split up into several phases cannot coexist in equilibrium with a thermodynamically stable one-phase system. The special problem of equilibration of a closed composite thermodynamic system with internal adiabatic constraints is considered. Finally, the equilibration of a thermodynamic system interacting with some large reservoirs is discussed.

2. MATHEMATICAL PRELIMINARIES

In this section the basic terminology and results of convex analysis in several real variables (which is the required setting for equilibrium thermodynamics) will be summarized. For further explanation and for proofs we refer to the comprehensive account of convex analysis in several real variables given in the book by Rockafellar [8]. For an introduction to convex analysis on a more abstract level (namely, for normed linear spaces) see [10]. The basic terminology of convex analysis is explained in Section 2.1. The required results of convex analysis on minimization of convex functions are collected in Section 2.2. Section 2.1 will be used in Sections 4 and 5. Section 2.2 will be used in Section 5. Several thermodynamic results that will be described in this paper do not depend on convex analysis. For example, in Section 3 only the first few definitions given in Section 2.1 will be used (namely, those up to and including the definition of strict convexity); Section 3 is independent of the remainder of Section 2.

2.1. Convex Analysis

Convex analysis provides an alternative to the classical mathematical approach to extremum problems, in which differentiation plays a very important role. In thermodynamics, for example, the process of maximizing or minimizing a function of several variables is almost always identified with the process of putting some partial derivatives equal to zero. Generally, however, using this procedure one can also find local minima or maxima, or points that are not extrema but saddle points. If the function to be minimized is convex, or, analogously, if the function to be maximized is concave, then it is possible to get much more information about the points where the function attains its extrema. In order to describe the minimum points of convex functions more precisely, convex analysis makes use of several concepts and techniques. First, differentiation is replaced by a more general process, which is called "subdifferentiation." Second, there is a constant interplay in convex analysis between the functions to be minimized and their "conjugate functions." The main preliminary to be treated is the definition of a "closed" convex function. These concepts will be described in this section. As will be seen, convex conjugation is in fact an extension of the classical Legendre transformation process which is extensively used in equilibrium thermodynamics.

The basic setting is the n -dimensional real *Euclidean space* R^n , which consists by definition of all n -tuples $x = (x_1, \dots, x_n)$ of real numbers. Addition and multiplication with scalars in R^n are defined component-wise. That is, the sum of two vectors $x = (x_1, \dots, x_n)$ and $y = (y_1, \dots, y_n)$ in R^n is defined to be the vector $(x_1 + y_1, \dots, x_n + y_n)$; the product of the real number λ and the vector $x = (x_1, \dots, x_n)$ is defined to be the vector $(\lambda x_1, \dots, \lambda x_n)$. The distance between two vectors $x = (x_1, \dots, x_n)$ and $y = (y_1, \dots, y_n)$ in R^n is defined by the equation $|x - y| = \sqrt{(\sum_i |x_i - y_i|^2)}$. Given a vector x in R^n and a real number $r > 0$, the open ball with center at x and radius r is defined to be the set of all vectors y in R^n such that $|x - y| < r$. A subset C of R^n is said to be *open* if it contains an open ball around each of its elements. A subset C of R^n is said to be *closed* if its complement (i.e., the set of all vectors in R^n not contained in the set C) is open.

A subset C of R^n is called *convex* if it contains the line segment between each pair of its points, i.e., if for every pair of vectors x and y in C and for every real number λ such that $0 < \lambda < 1$, the vector $\lambda x + (1 - \lambda)y$ also belongs to C . A real-valued function f defined on a convex subset C of R^n is said to be *convex* if for all vectors x and y in C and for all real numbers λ such that $0 < \lambda < 1$ the inequality

$$f(\lambda x + (1 - \lambda)y) \leq \lambda f(x) + (1 - \lambda)f(y) \quad (2)$$

holds. A function f is said to be *concave* if its opposite, the function defined by $(-f)(x) = -f(x)$ for all x , is convex. As an important particular case of convexity, the real-valued function f defined on a convex subset C of R^n is said to be *strictly convex* if for all distinct vectors x and y in C and for all real numbers λ such that $0 < \lambda < 1$ the inequality (2) holds strictly:

$$f(\lambda x + (1 - \lambda)y) < \lambda f(x) + (1 - \lambda)f(y).$$

There are many formal advantages if convex functions are thought to be defined throughout R^n , in the following way. A convex real-valued function f , which is originally defined on a convex subset C of R^n , is extended to all of R^n by giving f an infinite value outside of C :

$$f(x) = \infty \quad (x \notin C).$$

Hence from now on, convex functions defined on R^n have real or infinite values. Arithmetic involving the number ∞ presents no special difficulties: the forbidden subtraction $\infty - \infty$ is more or less automatically avoided by the theory. For functions that can assume infinite values, the formal definition of convexity, in terms of epigraphs, will now be given. For a function f defined on R^n whose values are real or ∞ or $-\infty$, the *epigraph* of f is defined to be the set of points above the graph of f , i.e., the following subset of R^{n+1} :

$$\text{epi}(f) = \{(x, \mu) \mid x \in R^n, \mu \in R, \mu \geq f(x)\}.$$

A function f defined on R^n whose values are real or ∞ or $-\infty$, is said to be *convex* if its epigraph is a convex set. It is not difficult to verify that this definition is consistent with the definition of convexity of functions given in the preceding paragraph. A convex function f defined on R^n is said to be *proper* if there is at least one vector x in R^n such that $f(x)$ is finite, and if f nowhere takes the value $-\infty$. The *effective domain* of a proper convex function f , which is denoted by $\text{dom } f$, is defined to be the (convex) set of points where the value of f is finite. A smoothly operating minimization theory in terms of subdifferentiation and conjugacy is obtained if attention is given only to closed proper convex functions. A proper convex function defined on R^n is said to be *closed* if its epigraph is a closed set. (As an example, it may be verified with this definition that the convex function f_1 of one real variable, defined by $f_1(x) = 0$ for $-1 < x < 1$ and by $f_1(x) = \infty$ for $x \geq 1$ and $x \leq -1$, is not closed, and that the convex function f_2 defined by $f_2(x) = 0$ for $-1 \leq x \leq 1$ and by $f_2(x) = \infty$ for $x > 1$ and $x < -1$ is closed.) A proper convex function f defined on R^n is closed if and only if it is lower semi-continuous, i.e., if and only if the set $\{x \in R^n \mid f(x) > \lambda\}$ is an open subset of R^n for all real numbers λ [8, p. 52]. A proper convex function that is not closed has very unnatural discontinuities. With any proper convex function f defined on R^n is associated in a certain way a unique closed proper convex function defined on R^n , which is called the *closure* of f and denoted by $\text{cl } f$. (In the example just mentioned, the closure of the convex function f_1 is f_2 .) In practical applications of convex analysis, including the thermodynamic applications that will be treated in this paper, it is very convenient to replace a given convex function by its closure. This does not change the function significantly, in the following sense. At all points of the relative interior of the effective domain of f , the values of the function f and its closure agree:

$$(\text{cl } f)(x) = f(x) \quad (x \in \text{ri}(\text{dom } f)).$$

Here, the *relative interior* (denoted by ri) of a subset C of R^n is defined to be the usual interior of C considered as a subset of the smallest affine subset of R^n containing C . (Affine sets form a subclass of the convex sets: by definition, an affine subset of R^n contains the complete line $\{\lambda x + (1 - \lambda)y \mid \lambda \in R\}$ through each pair x, y of its points.) For a proper convex function f defined on R^n , the value of the closure of f at an arbitrary point y is determined by the formula

$$(\text{cl } f)(y) = \lim_{\lambda \downarrow 0} f((1 - \lambda)y + \lambda x), \quad (3)$$

where x is an arbitrary vector in $\text{ri}(\text{dom } f)$ [8, p. 57].

With the help of these preliminaries we can now describe the main notions of convex analysis: conjugate functions and subdifferentiation. The *conjugate* f^* of a proper convex function f defined on R^n is defined by

$$f^*(x^*) = \sup\{(x, x^*) - f(x) \mid x \in R^n\} \quad (x^* \in R^n). \quad (4)$$

In words, the value of the conjugate function f^* at the point x^* is defined to be the least upper bound (supremum) of the set of numbers $(x, x^*) - f(x)$, as x ranges over R^n . The (standard) inner product of two vectors $x = (x_1, \dots, x_n)$ and $y = (y_1, \dots, y_n)$ in R^n is defined by $(x, y) = \sum_i x_i y_i$. For many concepts of convex analysis there is a strong geometrical motivation underlying the formal definition. A concrete geometrical interpretation of Eq. (4) is as follows. In one dimension the variable x^* can be interpreted as the slope of a straight line m through the origin. Then, the (possibly negative) number $f^*(x^*)$ is the largest vertical "distance" between the line m and the graph of the function f (see Fig. 1a). Equivalently, the number $f^*(x^*)$ can be interpreted as the negative intercept of the "lowest" straight line n with slope x^* that intersects the graph of the function f (see Fig. 1b). The latter interpretation coincides (except for sign) with the geometrical interpretation of Legendre transforms of differentiable functions that is usually given in textbooks on thermodynamics: viewing the graph of a differentiable function f of a real variable x as the envelope of a family of tangent lines, the Legendre transform $\Psi(P)$ of f is the intercept Ψ of the tangent lines as a function of the slope P of the tangent lines [5, Section 5.2]. It is thus seen that convex conjugation is a generalization of the classical Legendre transformation process. Some technical details of the correspon-

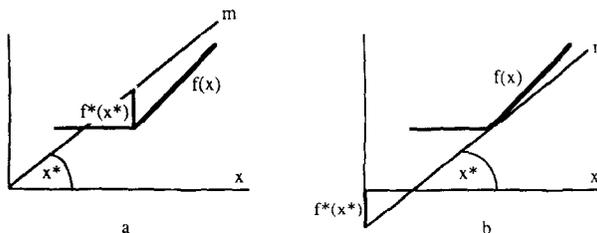


FIG. 1. Convex conjugation.

dence between convex conjugation and Legendre transformation will be given in Section 4.

The main facts about conjugate convex functions are as follows. The conjugate of a proper convex function defined on R^n is again a proper convex function, which is always closed. The operation of conjugacy $f \rightarrow f^*$ is actually a symmetric one-to-one correspondence in the class of all closed proper convex functions defined on R^n [8, p. 104]. Thus, if the proper convex function f defined on R^n is closed, then taking the conjugate of the conjugate f^* gives back the function f itself: $f^{**} = f$. (For arbitrary proper convex functions f defined on R^n , the formulas $(cl f)^* = f^*$ and $f^{**} = cl f$ hold.)

As a concrete example of convex conjugate functions, we mention here that the convex conjugate function f^* of the closed proper convex function f defined by $f(x) = e^x$ for all real numbers x , is given by $f^*(x^*) = x^* \ln x^* - x^*$ ($x^* > 0$), $f^*(0) = 0$, $f^*(x^*) = \infty$ ($x^* < 0$). This example shows that if a convex function takes only real values, then its conjugate may very well have infinite values.

Given a convex function f defined on R^n and a vector x in R^n , the *subdifferential* $\partial f(x)$ at a point x is defined to be the set of all *subgradients* of f at x , i.e., the set of all vectors x^* such that the inequality

$$f(z) \geq f(x) + (x^*, z - x) \tag{5}$$

holds for all vectors z in R^n . The standard concept of differentiation has, of course, a geometrical interpretation in terms of slopes of tangent lines. The concept of subdifferentiation, defined by (5), also has a geometrical interpretation. For example, let the graph of a convex function f of one real variable x consist of two linear pieces, as in Fig. 2. Then the subdifferential $\partial f(p)$ of the function f at the point $x = p$ where the two linear pieces of the graph meet, is equal to the set of all slopes of the straight lines through the point $(p, f(p))$ that are below the graph of f (see Fig. 2).

The subdifferential $\partial f(x)$ of a proper convex function f at a point x is always a closed convex subset of R^n , which might be empty. Defining the set

$$\text{dom } \partial f = \{x \in R^n \mid \partial f(x) \text{ is nonempty}\},$$

the following general inclusions hold for any proper convex function f [8, p. 217]:

$$\text{dom } f \supset \text{dom } \partial f \supset \text{ri}(\text{dom } f).$$

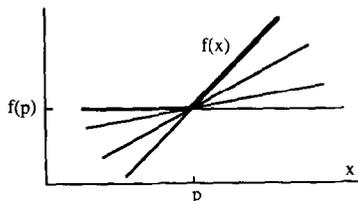


FIG. 2. Subdifferentiation.

(The relative interior (ri) of a set was defined before Eq. (3).) It is thus seen that a proper convex function f is always subdifferentiable in a large part of its effective domain ($\text{dom } f$), but never outside of $\text{dom } f$. As an example, the graphs of the subdifferential mappings of some particular (one-dimensional) closed proper convex functions are given in Fig. 3.

The relation between subdifferentiation and ordinary differentiation of convex functions will now be described briefly. A real or infinite-valued function f defined throughout R^n is said to be *differentiable* at a point x if $f(x)$ is finite and if there exists a vector x^* in R^n such that

$$\lim_{z \rightarrow x} \frac{f(z) - f(x) - (x^*, z - x)}{|z - x|} = 0;$$

if such a vector x^* exists, then it is unique and denoted by $\nabla f(x)$ (the *gradient* of f at x). The length $|x|$ of a vector $x = (x_1, \dots, x_n)$ in R^n is defined by $|x| = \sqrt{(\sum_i |x_i|^2)}$. For a convex function f at a point x where f is finite, the gradient $\nabla f(x)$ exists if and only if the ordinary (two-sided) partial derivatives of f exist at x ; then, the i th vector-component of $\nabla f(x)$ is simply the i th partial derivative of f at x . The relation between ordinary differentiation and subdifferentiation can be expressed as

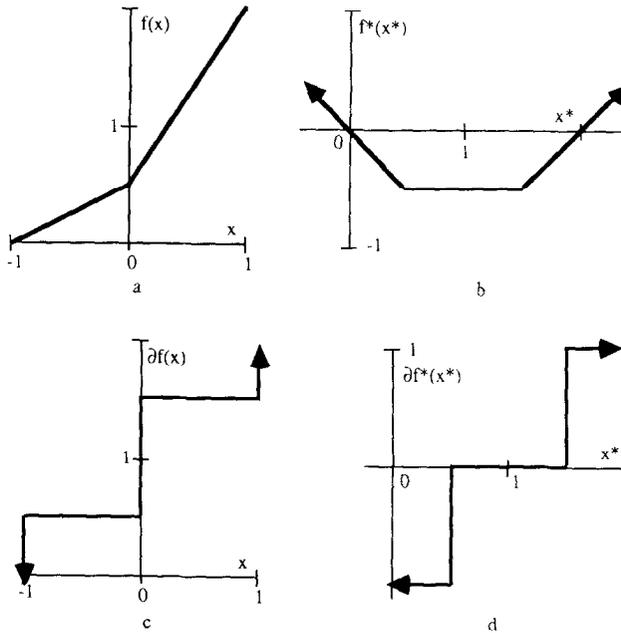


FIG. 3. Conjugates and subdifferentials of convex functions. Line segments ending with an arrow should be regarded as extended indefinitely in the given direction. (a) The original function f , $f(x) = x$ for $x < -1$ and $x > 1$. (b) The conjugate function f^* . (c) The subdifferential ∂f . $\partial f(x)$ is empty for $x < -1$ and $x > 1$ and multivalued for $x = -1, 0, 1$. (d) The subdifferential ∂f^* . $\partial f^*(x^*)$ is multivalued for $x^* = \frac{1}{2}$ and $x^* = \frac{3}{2}$.

follows: a convex function f is differentiable at a point x where it is finite if and only if f has a unique subgradient x^* at x ; in this case, the unique subgradient equals $\nabla f(x)$ [8, p. 242].

Several of the definitions and results of convex analysis described in this section and the next section are illustrated in Fig. 3.

2.2. Minimization of Convex Functions

In this section a brief summary is given of the required general results of convex analysis concerning the minimization of convex functions. Extensive use will be made of the terminology and notation described in the previous section.

As may be verified with the definitions given in the previous section, the following three conditions are equivalent for any proper convex function f defined on R^n [8, p. 218]:

$$\begin{aligned} x^* \in \partial f(x) \\ (z, x^*) - f(z) \text{ attains its supremum in } z \text{ at } z = x \\ f(x) + f^*(x^*) = (x, x^*). \end{aligned} \quad (6)$$

From the definition of convex conjugation (see Eq. (4)) it follows that for each proper convex function f defined on R^n and for all vectors x and x^* in R^n the inequality $f(x) + f^*(x^*) \geq (x, x^*)$ holds. The equivalence of the conditions given in (6) shows that the subgradients of a proper convex function f at x are precisely the points where this inequality is an equality. The equivalence of the first two assertions in (6) will be used in a discussion of some thermodynamic minimization problems in Sections 4 and 5.

Subdifferential mappings of convex functions are multivalued functions, since the sets $\partial f(x)$ may contain more than one point (cf. Fig. 3c). It is an important fact that for a closed proper convex function f defined on R^n , the subdifferential mapping ∂f^* is the inverse of ∂f in the sense of multivalued functions [8, p. 218]. That is, for a closed proper convex function f defined on R^n the equivalence

$$x^* \in \partial f(x) \quad \text{if and only if} \quad x \in \partial f^*(x^*) \quad (7)$$

holds. This follows from the equivalence of the first and third assertions stated in (6) and from the fact that for closed proper convex functions f , the relation $f^{**} = f$ holds. As an example of the property of subdifferential mappings of conjugate closed proper convex functions expressed in (7), note that the graph of the subdifferential mapping ∂f^* of Fig. 3d is precisely the mirror image of the subdifferential mapping ∂f of Fig. 3c, in the diagonal line between the positive axes.

For an arbitrary real or infinite-valued function f defined on R^n , the set of vectors x in R^n such that $f(z) \geq f(x)$ for all vectors z will be called the *minimum set* of f : a function assumes its global minimum in each point of its minimum set. The points where a function attains its minimum (i.e., the elements of the minimum set)

will be called *minimum points*. In a theory of minimization it is obviously of interest to get as much information as possible on minimum sets. By the definition of subgradient (see (5)), the vector x is a minimum point of a convex function f defined on R^n if and only if 0 belongs to the subdifferential $\partial f(x)$. This is a generalization of the classical statement that in an extremum the partial derivatives are equal to zero. Using the equivalence given in (7), it also follows that for closed proper convex functions the minimum sets can be characterized explicitly: the minimum set of a closed proper convex function f defined on R^n is exactly equal to the set $\partial f^*(0)$. Hence many minimization problems can in principle be solved by the computation of convex conjugates and subdifferentials. It follows generally that the minimum set of a closed proper convex function is a closed convex set. Furthermore, a closed proper convex function attains its minimum if and only if its conjugate is subdifferentiable at 0 . It makes sense to look for a (global) minimum of a closed proper convex function f only if it is bounded below, which is true if and only if $0 \in \text{dom } f^*$, since, by the definition of conjugation (see Eq. (4)), we have $\inf f = -f^*(0)$. The fact that $0 \in \text{dom } f^*$ is not sufficient for the existence of a minimum point of f , is shown by the convex function $f(x) = e^x$ on the real line (the convex conjugate of the function e^x has been given in Section 2.1). As another example, reconsider the conjugate closed proper convex functions f and f^* of Fig. 3. The function f assumes its minimum only at -1 , which is precisely the derivative of the function f^* at 0 . Conversely, the minimum set of f^* is the closed interval $[\frac{1}{2}, \frac{3}{2}]$, which coincides with the subdifferential of f at 0 .

Here are a few additional general results which describe somewhat more precisely the minimum sets $\partial f^*(0)$ of closed proper convex functions f defined on R^n [8, p. 264]. The minimum set of a closed proper convex function f defined on R^n is nonempty if $0 \in \text{ri}(\text{dom } f^*)$; it is nonempty and bounded if and only if $0 \in \text{int}(\text{dom } f^*)$ (the interior of a subset C of R^n , i.e., the largest open set it contains, is denoted by $\text{int}(C)$); it contains a unique vector x if and only if f^* is differentiable at 0 , and then the expression $x = \nabla f^*(0)$ holds. The following fact was already known before the advent of convex analysis: a real-valued function defined on a convex subset of R^n can have at most one minimum point if this function is strictly convex (i.e., if strict inequality holds in the definition of convexity given by Eq. (2)).

In the application of the general results on minimum sets of convex functions found by convex analysis it is of interest to have general information about the subdifferential mappings of closed proper convex functions defined on R^n . By definition, the *graph* of the subdifferential ∂f of a convex function f is the set of all pairs of vectors x and x^* such that $x^* \in \partial f(x)$. According to convex analysis, the graphs of the subdifferential mappings of the closed proper convex functions defined on the real line R (i.e., dimension one) are precisely the complete non-decreasing curves (cf. Figs. 3c and 3d) [8, p. 232]. The following result holds for the graph of the subdifferential mapping of a closed proper convex function f defined on R^n (i.e., dimension arbitrary): the mapping $(x, x^*) \rightarrow x + x^*$ is a homeomorphism (i.e., one-to-one, onto, and continuous in both directions) from

the graph of ∂f to R^n [8, p. 340]. This result implies, among other things, that for a closed proper convex function f defined on R^n the statements $x^* \in \partial f(x)$ and $x \in \partial f(x^*)$ cannot hold simultaneously for distinct vectors x and x^* in R^n .

3. FUNDAMENTAL ENERGY FUNCTIONS AND THERMODYNAMIC STABILITY

In this section the basic properties of fundamental energy functions of thermodynamic systems will be studied. In addition the theory of thermodynamic stability will be considered. We shall restrict our attention to "normal" thermodynamic systems, i.e., those covered by the theoretical scheme treated in [5]. Hence special thermodynamic systems such as those involving negative temperatures [11], or "nonextensive systems" such as black holes [12] are excluded from the present considerations. (As a matter of fact, it has been concluded that in the thermodynamics of black holes fundamental entropy functions are not necessarily concave [13].) In this section only the first few mathematical definitions given in Section 2 will be used (namely, those up to and including the definition of strict convexity).

The assumption of positivity of temperatures ensures the equivalence of the maximum entropy principle and the minimum energy principle [5, Chap. 5]. Therefore, it is equivalent to relate the concavity properties of fundamental entropy functions to the maximum entropy principle, or to relate the convexity properties of fundamental energy functions to the minimum energy principle. For an argument relating the concavity of fundamental entropy functions directly to the maximum entropy principle, see Wightman [14]. Here, the convexity of fundamental energy functions will be derived in a different way from the minimum energy principle.

The fundamental energy function

$$U = U(X_1, \dots, X_n) \quad (8)$$

gives the values of the internal energy U of a thermodynamic system as a function of the values of a set of independent extensive parameters X_1, \dots, X_n that characterize the equilibrium states of the system completely, and that include the entropy of the system. It should be stressed that the domain of a fundamental energy function is a set of equilibrium states of a thermodynamic system. States of thermodynamic systems that are not equilibrium states, such as metastable states and unstable states (e.g., supercooled liquids), will not be considered. It will be convenient to denote the equilibrium states X_1, \dots, X_n simply as n -dimensional vectors $x = (x_1, \dots, x_n)$. The equilibrium states x of a thermodynamic system will be assumed to form a convex subset C of n -dimensional real Euclidean space R^n . In many cases the complete set of independent extensive parameters X_1, \dots, X_n describing the equilibrium states of a thermodynamic system, can assume either only nonnegative real values, or all real values. For example, mole numbers and volume cannot be negative. On the other hand, for example, the extensive parameters that describe

magnetic or electric properties (i.e., certain components of magnetic or electric moments [5, Chap. 14]) can assume all real values. As will be described in detail later in this section, we adopt a “global” view of fundamental energy functions: in some equilibrium states in the domain of a fundamental energy function U , the system may be split up into different phases. In this section the boundary points of the domain of the fundamental energy function U will be ignored; therefore, the set of equilibrium states forming the domain of U is assumed to be an open convex subset of R^n .

In order to show that the fundamental energy function U of a normal thermodynamic system is convex, suppose it is not convex. Then there exist equilibrium states x and y in the domain of U and a real number λ between 0 and 1 such that

$$U(\lambda x + (1 - \lambda)y) > \lambda U(x) + (1 - \lambda)U(y).$$

Using the extensivity of the internal energy, $U(\lambda x) = \lambda U(x)$, it follows that

$$U(\lambda x + (1 - \lambda)y) > U(\lambda x) + U((1 - \lambda)y).$$

This shows that if the thermodynamic system is in the equilibrium state $\lambda x + (1 - \lambda)y$, then the value of the total internal energy can become strictly lower at constant total entropy if the system is split up into two systems with states λx and $(1 - \lambda)y$ (one of the coordinates of these vectors stands for entropy). Hence, according to the minimum energy principle, the state $\lambda x + (1 - \lambda)y$ cannot exist as an equilibrium state, in contradiction to the definition of equilibrium states (which will be discussed below). This shows that the convexity of fundamental energy functions of normal thermodynamic systems follows from the minimum energy principle. Equivalently, the concavity of fundamental entropy functions follows from the maximum entropy principle. Hence the convexity of the fundamental energy functions of normal thermodynamic systems is a consequence of the second law of thermodynamics. If a concrete normal thermodynamic system were found whose fundamental energy function is not convex, then either the states in the domain of this fundamental energy function would not be genuine equilibrium states, or the minimum energy principle would not be generally valid in the form in which it is usually stated. Given a function U giving the internal energy of a normal thermodynamic system, it is reasonable to define *equilibrium states* of this system, in accordance with the minimum energy principle, to be states x in the domain of U for which there do not exist distinct states x_1 and x_2 in the domain of U such that $x = x_1 + x_2$ and $U(x) > U(x_1) + U(x_2)$. Using this definition, it follows that a function giving the internal energy of a thermodynamic system is convex if and only if all states in its domain are equilibrium states, i.e., if and only if it is a fundamental energy function.

The convexity of fundamental energy functions is fundamental in equilibrium thermodynamics and will be used in much of what follows. An important special case of convexity is strict convexity (see the definition following Eq. (2) in Section 2.1). Stability of equilibrium states is directly related to a strict convexity property

of fundamental energy functions. However, the full fundamental energy function of a thermodynamic system is never strictly convex. This can be seen as follows. If the (convex) fundamental energy function of a thermodynamic system were strictly convex, then there would not exist distinct equilibrium states x and y in the domain of U and a real number λ satisfying $0 < \lambda < 1$, such that $U(\lambda x + (1 - \lambda)y) = \lambda U(x) + (1 - \lambda)U(y)$. For an arbitrary equilibrium state x , however, the extensivity property implies, for example, $U(2x) = 2U(x)$ and $U(3x) = 3U(x)$, which yield $U(2x) = (U(x) + U(3x))/2$, so the fundamental energy function U is in general not strictly convex.

The simplest way to exclude this trivial way of splitting up a thermodynamic system is the standard procedure of keeping one of the independent extensive parameters describing the equilibrium states systematically constant. This constant parameter will often be dropped from the list of independent variables. For example, the volume of the system or the total mole number might be kept constant. Denoting the constant independent extensive parameter by x_n , the equilibrium states $x' = (x_1, \dots, x_{n-1})$ in the resulting (smaller) domain of a fundamental energy function will in this section be distinguished by using primes. Of course, the resulting restriction of a fundamental energy function is still convex. If such a restriction of a fundamental energy function of a thermodynamic system is not strictly convex, then there exist distinct equilibrium states x' and y' and a real number λ satisfying $0 < \lambda < 1$, such that

$$U(\lambda x' + (1 - \lambda)y') = \lambda U(x') + (1 - \lambda)U(y').$$

Again denoting the (constant) value of the n th independent extensive parameter by x_n and using the extensivity of U , it follows that

$$U(\lambda x' + (1 - \lambda)y', x_n) = U(\lambda x', \lambda x_n) + U((1 - \lambda)y', (1 - \lambda)x_n).$$

Hence the equilibrium state $(\lambda x' + (1 - \lambda)y', x_n)$ may not be homogeneous: if the system is in this state, then it might spontaneously split up into two systems with states $(\lambda x', \lambda x_n)$ and $((1 - \lambda)y', (1 - \lambda)x_n)$, since this would not increase the total energy, and the total entropy would remain constant. The total value of the independent extensive parameters in such a split-up state is, however, still given by the vector $(\lambda x' + (1 - \lambda)y', x_n)$. By the convexity of a fundamental energy function, all equilibrium states in its domain, including those in which the system is split up into different phases, are "stable," in the sense that the total energy cannot be made strictly lower at constant total entropy by (further) splitting up the system. However, it is desirable to consider a narrower definition of thermodynamic stability, in order to partition the set of all equilibrium states in the domain of the fundamental energy function of a thermodynamic system into disjoint subsets, depending on the phase behavior of the system. The most natural formal definition of *thermodynamic stability* seems to be the following: an equilibrium state x' of a thermodynamic system is thermodynamically stable if it has an open convex neighborhood (in R^{n-1}) on which the (restriction of the) fundamental energy

function U is strictly convex. Of course, the same definition of thermodynamic stability can also be applied to situations in which more than one independent extensive parameter is held constant.

This definition of thermodynamic stability can be illustrated with a simple analogy from mechanics. Suppose that a marble is constrained to move in a vertical plane on a form given by a convex function f having a minimum at $x=0$ (see Fig. 4). Then the final equilibrium state $x=0$ is stable if and only if the convex function f is strictly convex on an open convex neighborhood of $x=0$. We have assumed the function f of Fig. 4 to be convex because the corresponding function from equilibrium thermodynamics, the fundamental energy function, is convex for normal thermodynamic systems, as has been shown above.

It is clear that equilibrium states that are not thermodynamically stable in this sense are related to phase transitions and critical phenomena. There has been some confusion in the literature as to the behavior of fundamental energy functions in connection with phase transitions and critical phenomena. For example, Münster wrote that "it is not possible to represent the internal energy of, say, a mol of argon as a continuous function of volume and entropy around the transition points. For instance, there is a break in the function at the condensation point and the function thus cannot be defined for a certain range of the variables.... Of course, we can interpolate across this gap formally by introducing metastable states and unstable states. This process is often of practical importance but has no direct physical significance." [15] Following Gibbs, we adopt a more global view of fundamental energy functions. In fact, one of the reasons for the use of graphs of the function $U(S, V)$ for a fixed amount N of a one-component system, given by Gibbs in his first paper on thermodynamics, is that the properties of thermodynamic systems that are split up into different phases are most simply and clearly exhibited in such diagrams [1, p. 24]. (The graph of the function $U(S, V)$ coincides precisely with what Gibbs called the "surface of dissipated energy" [1, p. 24]. According to Gibbs, this surface is "everywhere concave upward except where it is plane" [1, p. 48]; this is a way of expressing the convexity of the function $U(S, V)$.) Following a customary approximation, the surface between the distinct phases of a thermodynamic system will not explicitly be taken into account in this paper. Then, of course, the physical significance of extensive variables such as the entropy and volume of a thermodynamic system that is split up into several phases, is that these are simply the sum of the values of these variables in the different phases. The way

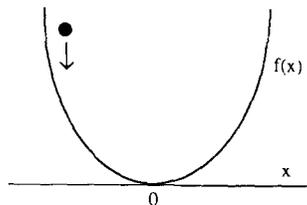


FIG. 4. Stability and strict convexity.

in which, for example, a fixed amount N of one-component system is split up into phases is uniquely determined by the function $U(S, V)$ and by the values of the total entropy S and volume V . The internal energy U of such a system, being a convex function of S and V , is also a continuous function of these variables. (A convex real-valued function defined on an open convex subset of R^n is always continuous [8, p. 82].)

We shall now give a characterization of equilibrium states that are not thermodynamically stable according to the definition given above. Again, one of the coordinates of the vectors x representing the equilibrium states of a thermodynamic system will be kept constant, and the remaining coordinates x' of the vectors x will be distinguished by using primes. A fundamental energy function U will be said to be *flat* on the convex subset C' of its domain if for all states y' and z' in C' and for all real numbers λ between 0 and 1, the following equality holds:

$$U(\lambda y' + (1 - \lambda) z') = \lambda U(y') + (1 - \lambda) U(z').$$

It is easily seen that an equilibrium state x' is not thermodynamically stable, i.e., the fundamental energy function U is not strictly convex in any open neighborhood of x' , if and only if each open neighborhood of x' contains straight line segments on which U is flat. In this case either the state x' itself is or is not contained in a line segment on which U is flat. Hence an equilibrium state x' of a thermodynamic system is not thermodynamically stable in the sense defined above if and only if one of the following two conditions is satisfied by x' :

There exists at least one straight line segment of length >0 and containing x' , on which U is flat. (9a)

Each open neighborhood of x' contains straight line segments of length >0 on which U is flat, but the state x' itself is not contained in such a line segment. (9b)

In the simplest case of the situation described in (9a), straight line segments on which U is flat, having length >0 and containing the state x' , exist only in precisely one direction. In such equilibrium states two phases coexist: supposing that in this case the longest line segment containing x' on which U is flat has endpoints y' and z' and choosing λ between 0 and 1 such that $x' = \lambda y' + (1 - \lambda) z'$, the state (x', x_n) stands for two coexisting systems ("phases") with states $\lambda(y', x_n)$ and $(1 - \lambda)(z', x_n)$ (this is precisely the lever rule of thermodynamic phase theory [5, Section 9.2]). Note that in this example the equilibrium states represented by the endpoints y' and z' satisfy condition (9a) and hence are multiphase states, although in these states the system consists of only one phase. As in this special case and in accordance with the usual procedures of thermodynamic phase theory, it will be assumed that equilibrium states satisfying (9a) are representative of systems that are split up into several phases. Equilibrium states x' that satisfy the condition given in (9a) will therefore be called *multiphase states*. The phase transitions involved in such mul-

tiphase states are first-order phase transitions. The precise way in which multiphase states are split up into phases will not be studied systematically and generally here; usually, the relative amounts of the different phases in a multiphase state can in principle be determined using constructions such as the lever rule. In addition to thermodynamically stable states and multiphase states, thermodynamic systems may exhibit a third kind of equilibrium states: critical points. Such states correspond to the condition given in (9b). Therefore, if an equilibrium state x' satisfies the condition given in (9b), it will be called a *critical point*. With these definitions, the above characterizations of equilibrium states that are not thermodynamically stable can be reformulated as follows: an equilibrium state x' is not thermodynamically stable if and only if it is either a multiphase state or a critical point. Note that if for an equilibrium state x' there exist two distinct states x'_1 and x'_2 (satisfying $x' = x'_1 + x'_2$) such that $U(x') = U(x'_1) + U(x'_2)$, then this state is a multiphase state. Hence critical points are stable equilibrium states in the sense that they cannot split up in this way, although critical points do not belong to the set of equilibrium states that are thermodynamically stable according to the definition given above. On the other hand, equilibrium states involving second and higher order phase transitions do belong to the class of equilibrium states that are thermodynamically stable in the sense defined here.

The treatment of thermodynamic stability given above uses only convexity properties of the fundamental energy function of a thermodynamic system. Ever since the time of Gibbs and Duhem, however, thermodynamic stability has usually been treated using differentiability properties of fundamental energy functions. In the standard treatments of thermodynamic stability, an important role is played by the quadratic form d^2U or, equivalently, by the Hessian matrix U_{ij} of the fundamental energy function U , which is defined by

$$U_{ij}(x) = \frac{\partial^2 U}{\partial x_i \partial x_j}(x)$$

for an arbitrary equilibrium state $x = (x_1, \dots, x_n)$ in the domain of U . The usual mathematical expression of thermodynamic stability is that the Hessian matrix of the fundamental energy function is strictly positive definite if one of the independent extensive parameters is held constant and suppressed from the list of variables (see, e.g., [5, Chap. 8 and 9, Appendix G; [16]). This characterization of thermodynamic stability, on which many thermodynamic inequalities are based, has often been regarded as one of the most basic theoretical facts of equilibrium thermodynamics. For example, the "inner product approach" to equilibrium thermodynamics as expounded by Weinhold is based entirely on the single assumption that the Hessian matrix of the fundamental energy function of a thermodynamic system is strictly positive definite (if, again, one of the independent extensive parameters is held constant and suppressed) [17]. However, the convexity properties of a fundamental energy function of a thermodynamic system seem to be a more global and deeper consequence of the laws of equilibrium thermodynamics

than the positive definiteness properties of Hessians of fundamental energy functions. The fundamental functions of equilibrium thermodynamics cannot always be assumed to be twice continuously differentiable, whereas convexity can always be defined without using any differentiability assumptions at all.

In the remainder of this section the relation between the convexity properties of a fundamental energy function and the positive definiteness properties of its Hessian matrix will be investigated. The main mathematical result relating the convexity properties of a function to the positive definiteness properties of its Hessian matrix is stated in the following theorem. Recall that a matrix A_{ij} is said to be *strictly positive definite* if for all nonzero vectors $y = (y_1, \dots, y_n)$ we have $\sum_{i,j} y_i A_{ij} y_j > 0$, and *positive semi-definite* if for all vectors y we merely have $\sum_{i,j} y_i A_{ij} y_j \geq 0$.

THEOREM 10. *A twice continuously differentiable real-valued function f defined on an open convex set C in R^n is convex if and only if its Hessian matrix, defined by $f_{ij}(x) = \partial^2 f / \partial x_i \partial x_j(x)$, is positive semi-definite for every vector $x = (x_1, \dots, x_n)$ in C [18].*

We shall also need a sharper result, which relates strict positive definiteness and strict convexity. One of the two assertions of Theorem 10 can be extended in this direction:

THEOREM 11. *If the Hessian matrix $f_{ij}(x)$ of a twice continuously differentiable real-valued function f defined on an open convex set C in R^n is strictly positive definite for all x in C , then f is strictly convex on C [18].*

The other half of Theorem 10 cannot be extended to relate strict positive definiteness and strict convexity: if the function f is strictly convex on C , then its Hessian matrix $f_{ij}(x)$ does not need to be strictly positive definite for all x in C . A simple counterexample in one dimension is given by the function $f(x) = x^4$. This function is strictly convex, but the value of its second derivative is once zero. Conditions that are necessary and sufficient for strict convexity of twice continuously differentiable functions have been given in [19].

The results stated in Theorems 10 and 11 allow the convexity or strict convexity of a function to be proved by the verification that a local property (i.e., positive semi-definiteness or strict positive definiteness of the Hessian matrix) holds at each point separately. These positive definiteness properties of a matrix are, in turn, related to certain properties of its principal minors. For convenience, these properties will now be summarized. Recall that the *principal minors* of an $n \times n$ matrix are the determinant of the matrix itself, and the determinants of all the matrices obtained when any number of rows and columns (bearing the same numbers) are crossed out. The *upper left principal minors* of the $n \times n$ matrix A_{ij} are the determinants $\det A_{ij}$ with $1 \leq i, j \leq k$, for $k = 1, \dots, n$.

THEOREM 12. *A symmetric $n \times n$ matrix with only real elements is positive semi-definite if and only if each of its principal minors is nonnegative [20].*

THEOREM 13. *A symmetric $n \times n$ matrix with only real elements is strictly positive definite if and only if all its upper left principal minors are strictly positive [21].*

A real symmetric $n \times n$ matrix is not positive semi-definite if and only if just all its upper left principal minors are nonnegative: a counterexample is given by the 2×2 matrix $\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$.

From the convexity of the fundamental energy function U of a thermodynamic system and Theorems 10 and 12, it follows that if U is twice continuously differentiable in an open convex neighborhood of the equilibrium state x , then all principal minors of the Hessian matrix $U_{ij}(x)$ are nonnegative. One of the principal minors of $U_{ij}(x)$ can be calculated explicitly and generally: for an arbitrary equilibrium state x where the fundamental energy function $U(x)$ is twice continuously differentiable, the determinant of the entire Hessian matrix $U_{ij}(x)$ is zero because of extensivity (see, e.g., [22]). Here is a simple thermodynamic proof of this fact. According to the Gibbs-Duhem equation, we have $\sum_j X_j dP_j = 0$, where the intensive parameters $\partial U / \partial X_j$ are denoted by P_j , and where the sum runs over all independent extensive parameters X_j . Expanding the differentials as $dP_j = \sum_i U_{ij} dX_i$, it follows that $\sum_{i,j} U_{ij} X_j dX_i = 0$. Varying each independent extensive parameter X_i separately, it follows that $\sum_j U_{ij} X_j = 0$ for all i . Hence by linear algebra, $\det U_{ij} = 0$.

As has already been mentioned above, the stability of a thermodynamic system is usually expressed mathematically by saying that the Hessian matrix of the fundamental energy function is strictly positive definite if one of the independent extensive parameters is held constant and suppressed from the list of variables. It will now be shown that this statement implies the definition of thermodynamic stability given above in terms of strict convexity. If an equilibrium state x' (this notation has been explained earlier in this section) is stable in the usual sense, then by continuity, the Hessian matrix of the fundamental energy function, $U_{ij}(y')$, is strictly positive definite in an open convex neighborhood of the state x' . Hence by Theorem 11, the fundamental energy function is strictly convex on an open convex neighbourhood of x' , so the state x' is thermodynamically stable in the sense defined above. However, the two definitions of thermodynamic stability are not completely equivalent. The usual definition of thermodynamic stability is a sufficient condition (as has just been shown), but it is not a necessary condition for thermodynamic stability in the sense defined here. The problem is that, as has already been mentioned, the converse of Theorem 11 does not hold. Nevertheless, the definition of thermodynamic stability given in this section is more reasonable from the physical point of view. Analogously, if in the mechanical example of Fig. 4 the function f is defined to be the strictly convex function $f(x) = x^4$, then it would not be concluded that the final equilibrium position $x = 0$ is not stable because of the fact that for $x = 0$ the second derivative of f is zero.

4. TRANSFORMED FUNDAMENTAL FUNCTIONS

The standard thermodynamic potentials of a thermodynamic system (for example, the enthalpy, the Helmholtz free energy, and the Gibbs free energy) are usually obtained from the fundamental energy function by means of a Legendre transformation process (see, e.g., [5, Section 5.2]). All equilibrium-thermodynamic information about a thermodynamic system is not only contained in a fundamental energy function, but also in these transformed functions, which will be referred to as *transformed fundamental functions*. In this section some mathematical aspects of the transformation from fundamental energy functions to functions such as the Gibbs free energy will be studied using convex analysis (see Section 2.1).

The generalization of the Legendre transformation process from one of the several variables is commonly held to be "simple and natural" [5, p. 95] and to "offer no difficulties except that of notation" [6, p. 62]. This is, however, not completely true. As an illustration of the difficulties, note that Legendre transformation of the fundamental energy function U with respect to several extensive variables X_1, \dots, X_k is often taken to be possible provided that the Jacobian $\partial(P_1, \dots, P_k)/\partial(X_1, \dots, X_k)$ does not vanish (the intensive parameters $\partial U/\partial X_i$ are denoted by P_i) (see, e.g., [6, p. 63]). The relevant mathematical result in this connection is the inverse function theorem [9, pp. 221–223], which guarantees the possibility of inversion of the equations $P_i = P_i(X_1, \dots, X_k)$ locally, that is, only in a (possibly very small) neighborhood of the point given by the coordinates X_1, \dots, X_k . As a matter of fact, "global" inversion (i.e., inversion of the complete function) may not be possible even if the Jacobian is nowhere zero. As a simple example of this phenomenon, consider the function of two real variables defined by $f(x, y) = (e^x \cos y, e^x \sin y)$ [9, Chap. 9, Exercise 19]. The Jacobian of this function is equal to e^x , hence it is nowhere zero. Yet, this function cannot be ("globally") inverted: adding 2π to y yields the same value of $f(x, y)$.

It would thus appear that because of the inverse function theorem, the Legendre transforms of equilibrium thermodynamics may be assumed to exist only locally. Nevertheless, thermodynamicists never speak of "local Legendre transforms." It will be shown in this section that the fact that the transformed fundamental functions of equilibrium thermodynamics may be assumed to exist globally, can be rigorously established when the convexity of fundamental energy functions is taken into account. (Similarly, convexity is essential in another theoretical-physical application of the Legendre transformation process, namely, the construction of Hamiltonians from Lagrangians in classical mechanics [23].)

In the general situation considered in the previous section, the (convex) fundamental energy function U of a thermodynamic system was assumed to be defined on a set of equilibrium states forming an open convex subset of R^n . Following the common practice of convex analysis (see Section 2.1), the fundamental energy function U will be extended to all of R^n by giving it the value ∞ on the complement of its domain and by replacing this extended function if necessary by its closure. In this way the fundamental energy function U becomes a closed proper convex

function defined throughout R^n . The effective domain of the fundamental energy function U is always n -dimensional, so its relative interior coincides with its (ordinary) interior. The interior of the effective domain of the fundamental energy function U coincides precisely with that was called the domain of U in Section 3. The value of U at the boundary of its effective domain can be determined by taking limits (see Eq. (3) in Section 2.1). The functions that are Legendre transformed in equilibrium thermodynamics are restrictions of the full fundamental energy function in which several independent extensive variables are kept constant. In the same way as just described for the full fundamental energy function, these restrictions of the fundamental energy function give rise to closed proper convex functions defined throughout a lower dimensional Euclidean space R^k . With this preparation, the process of convex conjugation described in Section 2.1 can be applied to the functions that are Legendre transformed in equilibrium thermodynamics. As has already been mentioned in Section 2.1, there is a strong connection between convex conjugation and Legendre transformation. We shall now describe this connection more precisely by stating some theorems from convex analysis.

The formal definition of Legendre transformation can be stated as follows. Suppose that f is a differentiable real-valued function defined on an open subset C of R^n . The *Legendre transform* of f is defined to be the function g (if it exists) whose domain D is the image of C under the gradient mapping ∇f , and which is defined by the formula

$$g(x^*) = ((\nabla f)^{-1}(x^*), x^*) - f((\nabla f)^{-1}(x^*)) \quad (14)$$

(see [8, p. 256]). For clarity, the domains of functions to be Legendre transformed are sometimes mentioned explicitly by writing the functions as pairs; for example, in the preceding definition, the Legendre transform of (C, f) is (D, g) . Remarkably, it is not necessary that the gradient mapping ∇f be one-to-one on C for the function g to be well defined. For this, it is sufficient that we merely have $(x_1, x^*) - f(x_1) = (x_2, x^*) - f(x_2)$ whenever $\nabla f(x_1) = \nabla f(x_2) = x^*$. Then, the value of the right-hand side of Eq. (14) is determined uniquely by replacing the set $(\nabla f)^{-1}(x^*)$ by any of the vectors it contains. Apart from sign, the definition given by Eq. (14) coincides with the standard definition of Legendre transforms given in texts on equilibrium thermodynamics. A fundamental existence theorem for Legendre transforms is given by convex analysis:

THEOREM 15. *Let f be any closed proper convex function defined on R^n such that the interior of its effective domain $C = \text{int}(\text{dom } f)$ is nonempty, and such that f is differentiable on C . Then the Legendre transform g of f is well defined. The domain D of g (i.e., the range of ∇f) is a subset of $\text{dom } f^*$, and g is the restriction of f^* to D [8, p. 256].*

This result shows that for convex functions the mathematical theory of Legendre transformation is completely subsumed by the mathematical theory of convex conjugation described in Section 2.1. In Section 2.1 it was stated that the operation of

conjugacy is a symmetric one-to-one correspondence in the class of all closed proper convex functions defined on R^n . According to the following theorem of convex analysis, the special operation of Legendre transformation forms a symmetric one-to-one correspondence in a much smaller class of convex functions, which are said to be "of Legendre type." A closed proper convex function f defined on R^n is said to be *of Legendre type* if it is differentiable at each point of and strictly convex on the interior of its effective domain $C = \text{int}(\text{dom } f)$, and if it is essentially smooth. A proper convex function f defined on R^n is said to be *essentially smooth* if $C = \text{int}(\text{dom } f)$ is nonempty, if f is differentiable throughout C , and if $|\nabla f(x_m)| \rightarrow \infty$ whenever a sequence of vectors x_m converges to a boundary point of C as $m \rightarrow \infty$.

THEOREM 16. *Suppose that f is a closed proper convex function defined on R^n . Let $C = \text{int}(\text{dom } f)$ and $C^* = \text{int}(\text{dom } f^*)$. Then (C, f) is a convex function of Legendre type if and only if (C^*, f^*) is a convex function of Legendre type. When these conditions hold, (C^*, f^*) is the Legendre transform of (C, f) and (C, f) is the Legendre transform of (C^*, f^*) . The gradient mapping ∇f is then one-to-one from the open convex set C onto the open convex set C^* , continuous in both directions, and $\nabla f^* = (\nabla f)^{-1}$ [8, p, 258].*

This is a precise statement of a conclusion that is usually made plausible in texts on thermodynamics, to the effect that the definition of Legendre transformation given by Eq. (14) can always be used to reconstruct the original function from its Legendre transform (see, e.g., [5, p. 94]). It would be interesting if from the laws of equilibrium thermodynamics information could be adduced that guarantees that the functions that are Legendre transformed in equilibrium thermodynamics are of Legendre type. Then, because of Theorem 16, the usual definition of Legendre transformation (Eq. (14)) could always serve as the proper formal definition of Legendre transformation for thermodynamic purposes. Even if the strict convexity condition were assumed to give no problems, however, the "boundary" condition of essential smoothness does not seem to be guaranteed by the laws of equilibrium thermodynamics. The only "boundary condition" imposed by equilibrium thermodynamics on the mathematical form of fundamental energy functions is the third law, which requires that the value of the temperature $T = \partial U / \partial S$ tends to zero only if the value of the entropy S tends to zero. The condition of essential smoothness is not guaranteed by the third law, however. In order to show that the functions that are Legendre transformed in equilibrium thermodynamics cannot in general be assumed to be of Legendre type, some special fundamental energy functions will now be considered. One of the simplest thermodynamic systems whose fundamental function is exactly known (the "hydrogen atom" of equilibrium thermodynamics), is blackbody radiation [24]:

$$U = bS^{4/3}V^{-1/3}; \quad (17)$$

b is a positive constant, defined by $(405/2048)^{1/3} \pi^{-5/3} chk^{-4/3}$, where c is the speed

of light, h the Planck constant, and k the Boltzmann constant. Another explicitly known fundamental function is that of a one-component ideal gas [5, p. 53]:

$$U = U_0(V/V_0)^{-2/3}(N/N_0)^{5/3} \exp 2/3R(S/N - S_0/N_0). \quad (18)$$

In these equations S is the entropy, V is the volume, N is the mole number, R is the gas constant, and U_0 , S_0 , V_0 , N_0 are certain positive constants. Equation (17) is exact, whereas Eq. (18) is only a classical approximation valid for higher temperatures. Equation (18) does not satisfy the third law. Both fundamental energy functions have restrictions that are not of Legendre type. For example, holding U constant at a strictly positive value in Eq. (17) and letting S tend to 0 shows that the temperature $T = \partial U/\partial S = 4/3bS^{1/3}V^{-1/3}$ does not tend to ∞ . Hence, although the restriction of the fundamental energy function given in Eq. (17) to S (holding V constant) is strictly convex, it is not essentially smooth and hence not of Legendre type.

From these considerations it follows that the class of convex functions of Legendre type is too small to contain all the functions that are Legendre transformed in equilibrium thermodynamics. Hence unless there exists a larger and thermodynamically appropriate class of convex functions in which the Legendre transformation process defined by Eq. (14) forms a symmetric one-to-one correspondence, the definition given by Eq. (14) is too narrow for the applications in equilibrium thermodynamics. This is not disastrous: it has already been mentioned in Section 2.1 that the original (geometrical) interpretation given in texts on thermodynamics of the Legendre transformation process coincides with the geometrical interpretation for the more general convex conjugation process. Hence the "correct" formal definition of the transformed fundamental functions of equilibrium thermodynamics requires Eq. (4) instead of Eq. (14). In view of Theorem 15, however, the definition given by Eq. (14) can be of use in equilibrium thermodynamics in calculations of convex conjugates, if it can be assumed that the convex function to be transformed is differentiable in the interior of its effective domain.

There are other reasons why the convex conjugation process defined by Eq. (4) is preferable to the Legendre transformation process defined by Eq. (14). Because of the possibility of phase transitions and critical phenomena, the ("global") fundamental energy function of a thermodynamic system might not be continuously differentiable throughout the interior of its effective domain. (However, by a general result of convex analysis mentioned in Section 2.1, a proper convex function defined on R^n is always subdifferentiable in the relative interior of its effective domain.) In any case, the transformed fundamental functions of equilibrium thermodynamics may not be continuously differentiable in all equilibrium states: for example, if the function $G(p, T)$ gives the Gibbs free energy of a fixed amount N of pure water, and if water boils at pressure p and temperature T , then, as is well known, G is not differentiable with respect to p and T in this state (the volume and entropy are discontinuous). For all normal thermodynamic systems, including those exhibiting phase transitions and critical phenomena, convex conjugation yields the correct "global"

formal definition of transformed fundamental functions. (The behavior of transformed fundamental functions in connection with phase transitions will be discussed more extensively later in this section.)

Examples such as those given in Eq. (17) and (18) allow more conclusions to be drawn about the mathematical properties of the fundamental energy functions of equilibrium thermodynamics. Consider, for example, the following result of convex analysis.

THEOREM 19. *The subdifferential mapping ∂f of a closed proper convex function f defined on R^n is single-valued if and only if f is essentially smooth [8, pp. 251–252].*

(The definition of essential smoothness was given just before Theorem 16.) The fundamental energy function of blackbody radiation (see Eq. (17)) is not essentially smooth, as can easily be shown. Hence Theorem 19 shows that its subdifferential mapping is genuinely multivalued. In this example, however, the multivaluedness of the subdifferential mapping can occur only at the boundary of the effective domain since in the interior of its effective domain the fundamental energy function given by Eq. (17) is continuously differentiable. All equilibrium states of blackbody radiation (Eq. (17)) and the classical ideal gas (Eq. (18)) are thermodynamically stable in the sense defined in Section 3, as can be verified by the detailed computation of principal minors of Hessians and by applying Theorems 11 and 13.

Since the definition of Legendre transformation used in equilibrium thermodynamics differs in sign from the definitions given by Eq. (4) and (14), the transformed fundamental functions of equilibrium thermodynamics are concave in the transformed variables. In order to state this more precisely, write the equilibrium states x in the domain of the fundamental energy function U as pairs of vectors $x = (x', x'')$, where x' stands for the extensive variables with respect to which the fundamental energy function U is to be transformed. The transformed fundamental function obtained by transforming the fundamental energy function U with respect to the primed variable x' will be denoted by $U[']$. For arbitrary fixed vectors x'' , the transformed fundamental function $U[']$ is the opposite of the convex conjugate of U with respect to x' (cf. Eq. (4) in Section 2.1):

$$U['](x'^*, x'') = -U^*(x'^*, x'') = \inf\{U(x', x'') - (x', x'^*) \mid x'\}. \quad (20)$$

It follows that this function is concave in the variable x'^* for each fixed value of x'' . It is of interest to know when the infimum in Eq. (20) is actually attained. Let x'^* and x'' have fixed values. By the equivalence of the first two assertions given in (6) (see Section 2.2), the infimum in Eq. (20) is attained in y' ,

$$U['](x'^*, x'') = U(y', x'') - (y', x'^*), \quad (21)$$

if and only if $x'^* \in \partial U(y', x'')$, where the subdifferential is taken with respect to y' . In particular, if the gradient of U with respect to x' exists in the state y' and is equal to x'^* , then Eq. (21) holds. For example, if U is flat in an open convex subset C' ,

having constant gradient x'^* in C' , then Eq. (21) holds for any vector y' in C' . For each fixed value of x'^* the function defined by Eq. (20) seems quite generally to be convex as a function of the remaining variable x'' . Functions of several variables that are convex in some variables and concave in the remaining variables are called "saddle functions." Without going into detail, we mention only that saddle functions have been extensively studied in convex analysis (see [8, Part VII]).

It is clear that the mathematical form of the transformed fundamental functions of equilibrium thermodynamics is more complicated than the mathematical form of the original fundamental energy functions. These transformed fundamental functions are applied, for example, in the determination of final equilibrium states of thermodynamic systems and of maximum work deliverable by thermodynamic systems, under conditions of constant and uniform intensive parameters. In applications such as these, transformed fundamental functions can be replaced by the mathematically simpler and actually more generally applicable nonflow availability functions (see Eq. (32) in the next section). The main physical reason for the introduction of transformed fundamental functions in equilibrium thermodynamics is, of course, the fact that one wants to be able to regard variables that are easily controllable in practice, such as pressure and temperature, as independent variables of a fundamental function, instead of variables such as volume and entropy. In a certain sense, however, physical information is lost in the transformation from fundamental energy functions to transformed fundamental functions. Consider as an example a fixed amount N of a one-component thermodynamic system with (convex) fundamental energy function $U(S, V, N)$. Taking, as in Eq. (20), the opposite of the convex conjugate of this function with respect to the variables S and V , one obtains the Gibbs free energy $G(p, T, N)$. (Formally, the independent variables of the function G are more properly denoted by V^* , S^* , N , instead of p , T , N . However, by Theorem 15 a subset of the values assumed by the pair (V^*, S^*) corresponds to values of the pair (p, T) .) As has been shown above, this fundamental function is concave as a function of pressure p and temperature T , for each fixed value of N . (The mole number N , which is assumed to be constant, will be suppressed.) Consider a first-order phase transition that takes place at a certain pressure p and temperature T . As has already been mentioned and as is well known, the values of S and V cannot be derived uniquely from $G(p, T)$, since this function cannot be differentiated with respect to p and T in states involving a first-order phase transition. All that can be said is that the value of the pair of variables (S, V) is an element of the superdifferential $\partial G(p, T)$; since G is concave as a function of the variables p and T , we speak of "superdifferentials," which can be defined in complete analogy to subdifferentials of convex functions (see Eq. (5) in Section 2.1). The multiphase states (S, V) , which form a flat part of the fundamental energy function $U(S, V)$ (cf. Section 3), collapse into one point (p, T) at which the graph of the fundamental function $G(p, T)$ has an "angle" (cf. the pair of conjugate convex functions given in Fig. 3). For such states involving first-order phase transitions, the relation $G = U + pV - TS$ holds for arbitrary pairs of values (S, V) in a convex set where U is flat, as has been shown above (see Eq. (21)). In addition, it

follows that if we know only the function $G(p, T)$ and the values of p and T at which a first-order phase transition takes place, then we do not know the amounts of the different phases into which the system is divided. On the other hand, this information is implicitly known (by constructions such as the lever rule) if we know the function $U(S, V)$ and the values of S and V in a multiphase state (cf. Section 3). In this sense, some physical information is lost in the transformation of the fundamental energy function $U(S, V)$ to the Gibbs free energy $G(p, T)$. Hence transformed fundamental functions such as the Gibbs free energy are somewhat "less fundamental" than fundamental energy functions. Of course, this physical inequivalence of fundamental energy functions and transformed fundamental functions does not contradict the fact that fundamental energy functions can be completely reconstructed from transformed fundamental functions.

This section will now be concluded with a discussion of the convex conjugates of the full fundamental energy function of a thermodynamic system. It is well known in equilibrium thermodynamics that the Legendre transform of a fundamental energy function with respect to all its independent extensive variables is identically zero, as follows from the Euler relation. Let us consider the corresponding result from convex analysis. Because of the extensivity property, the fundamental energy functions of equilibrium thermodynamics are positively homogeneous. A real or infinite-valued function f defined on R^n is said to be *positively homogeneous* if for every vector x in R^n and for every real number $\lambda > 0$ one has $f(\lambda x) = \lambda f(x)$. Hence the fundamental energy functions of normal thermodynamic systems can be regarded as positively homogeneous closed proper convex functions defined on R^n . Such functions are characterized by the following result of convex analysis:

THEOREM 22. *A closed proper convex function f defined on R^n is positively homogeneous if and only if it is the support function of a nonempty closed convex subset C of R^n . For such functions f the set C is characterized by $C = \{x^* \mid (x, x^*) \leq f(x) \text{ for all } x\}$ [8, p. 114].*

The *support function* δ_C^* of a convex subset C of R^n is defined by

$$\delta_C^*(x^*) = \sup\{(x, x^*) \mid x \in C\} \quad (x^* \in R^n). \quad (23)$$

It is easily seen that the support function δ_C^* is the convex conjugate of the *indicator function* δ_C , which is defined by

$$\begin{aligned} \delta_C(x) &= 0 & (x \in C) \\ \delta_C(x) &= \infty & (x \notin C). \end{aligned} \quad (24)$$

In turn, the convex conjugate of the support function δ_C^* of a closed convex set C is precisely the indicator function δ_C of this set. It follows that the convex conjugate of

the full fundamental energy function of a thermodynamic system is the indicator function of a nonempty closed convex subset C of R^n :

$$U^* = \delta_C. \quad (25)$$

In this sense, the Legendre transform of the fundamental energy function of a thermodynamic system with respect to all its independent extensive variables is indeed identically zero.

By Theorem 22, the fundamental energy function U of a thermodynamic system can be represented as the support function $U = \delta_C^*$ of a closed convex subset C of R^n . In this way all physical information contained in a fundamental energy function having as independent variables a complete set of n independent extensive parameters is also contained in an n -dimensional closed convex set. It is interesting to look for a physical interpretation for the multidimensional closed convex sets that are associated in this way with the fundamental energy functions of equilibrium thermodynamics. If it is assumed that the fundamental energy function U of a normal thermodynamic system is differentiable in the interior of its effective domain, then by Theorem 15 it follows that the range of the gradient mapping ∇U is contained in the effective domain of the convex conjugate U^* of U , i.e., the set C of Theorem 22. The range of ∇U is precisely the set of values that can be assumed by the intensive parameters of the system. However, the range of the gradient mapping ∇U is usually a strictly smaller set than the closed convex set C of the representation $U = \delta_C^*$. Consider, for example, blackbody radiation (see Eq. (17)). In this case the pressure and temperature are related by the equation $p = aT^4$, where a is a positive constant. Hence the range of ∇U is in this example not convex, so it is contained in but not equal to the convex set C of the representation $U = \delta_C^*$.

There is a relation between the boundary of the closed convex set C of the representation $U = \delta_C^*$ of a fundamental energy function and the subgradients of U [25]. As will now be shown, the set of subgradients of U is a subset of the boundary of C . In order to prove that the range of the subdifferential mapping ∂f of a positively homogeneous closed proper convex function $f = \delta_C^*$ is a subset of C , suppose that $x^* \in \partial f(x)$. Then it follows that $f(x) + f^*(x^*) = (x, x^*)$ (see (6)). Hence $x^* \in C$; if $x^* \notin C$, then we would have $f^*(x^*) = \infty$. It follows also that if f is a positively homogeneous closed proper convex function and if $x^* \in \partial f(x)$, then

$$f(x) = (x, x^*). \quad (26)$$

This equation shows that if the subgradient $x^* \in \partial f(x)$ were an element of the interior of the set C of the representation $f = \delta_C^*$, then a distinct vector $y \in C$ that is collinear with x^* could be found such that $(x, y) > f(x)$; this would contradict Theorem 22. It is thus proved that the subgradients of a fundamental energy function $U = \delta_C^*$ of a thermodynamic system lie on the boundary of the set C . It seems that in general there may be boundary points of C that are not subgradients of $U = \delta_C^*$; for example, if (a restriction of) a fundamental energy function U converges asymptotically to an affine function (i.e., a function that differs from a linear

function only by a constant), then the set of subgradients of U may not be closed.

Using Theorem 22 a general thermodynamic inequality can be obtained. Denoting the gradient mapping ∇U by P and using inner product notation, the Euler relation of equilibrium thermodynamics can be stated as

$$U(x) = (P(x), x). \quad (27)$$

Equation (27) follows from Eq. (26) for arbitrary states x where U is differentiable. It follows also from the preceding considerations that if $f = \delta_C^*$ is a positively homogeneous closed proper convex function defined on R^n and if x^* is any subgradient of f , then for all x we have the inequality

$$f(x) \geq (x^*, x). \quad (28)$$

For example, if y is a state where a fundamental energy function U is differentiable then for all x the following inequality related to the Euler relation (27) holds:

$$U(x) \geq (P(y), x). \quad (29)$$

This thermodynamic inequality follows generally from the convexity of fundamental energy functions, and is related to a stability criterion given by Gibbs [1, p. 100].

5. THE MINIMUM ENERGY PRINCIPLE

One of the existing forms of Gibbs' characterization of thermodynamic equilibrium is the minimum energy principle (see, e.g., [5, Section 5.1]). In this section the existence and uniqueness of possible final equilibrium states of closed composite thermodynamic systems will be discussed on the basis of the minimum energy principle. Use will be made of several results of convex analysis on minimum points of convex functions (see Section 2.2).

Suppose that two thermodynamic systems with fundamental energy functions U_1 and U_2 are completely separated from their environment and are allowed to interact with each other through a separation S (see Fig. 5). These thermodynamic systems will be called System 1 and System 2, respectively. The separation S is "permeable" to several independent extensive parameters that are common to both thermodynamic systems, and which will be viewed as an n -dimensional vector variable x . For System 1 the value of this variable will simply be denoted by x , and the sum of the values of these extensive variables for Systems 1 and 2 will be denoted by $x_;$

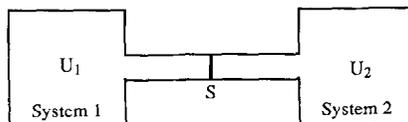


FIG. 5. A composite thermodynamic system.

this sum-vector x_i is assumed to be constant. For example, if one of the coordinates of x specifies the volume of System 1, then the separation S is a movable piston which is possibly permeable to other independent extensive variables as well. According to the minimum energy principle, the final equilibrium state x reached by this closed composite system will minimize the total internal energy:

$$U_i(x) = U_1(x) + U_2(x_i - x). \quad (30)$$

In Eq. (30) the independent extensive parameters of the two thermodynamic systems for which the separation S is not permeable are suppressed from the arguments of the fundamental energy functions U_1 and U_2 . These independent extensive parameters may not even be common to both systems, and their values are constant in both systems separately. Although some independent extensive variables have been suppressed from the vectors x and $x_i - x$, these "reduced" equilibrium states will in this section not be distinguished by means of primes, as was done in Section 3. In order to guarantee the separate identity of the two thermodynamic systems, both systems will be assumed to have at least one such constant independent extensive parameter for which the separation S is impermeable. As has been described in detail in the preceding sections, the fundamental energy functions U_1 and U_2 of Systems 1 and 2 will be regarded as closed proper convex functions defined on R^n . It follows that the function $x \mapsto U_2(x_i - x)$ is a closed proper convex function and also (by a result of convex analysis [8, p. 77]) that the function U_i defined by Eq. (30) is a closed proper convex function defined on R^n . Hence the techniques provided by convex analysis are applicable to thermodynamic extremum problems such as this. Using a result of convex analysis stated in Section 2.2, it follows that the possible final equilibrium states of the composite thermodynamic system depicted in Fig. 5 form a set of n -dimensional vectors that can be characterized explicitly as the subdifferential $\partial U_i^*(0)$ of the convex conjugate of the total energy function U_i at 0. Although actual numerical applications of this characterization to concrete composite thermodynamic systems would be complicated, it gives rise to some general conclusions about sets of possible final equilibrium states. For example, the set of possible final equilibrium states $\partial U_i^*(0)$ of a closed composite thermodynamic system is in general closed and convex. Hence if there exists more than one possible final equilibrium state, then there actually exists an uncountable infinity of such states. If there exists a unique final equilibrium state, then this state can in principle be found by calculating the gradient of the convex conjugate of the total internal energy function at 0: $\nabla U_i^*(0)$. If the function U_i defined by Eq. (30) can be assumed to be strictly convex, then there can be at most one final equilibrium state, but this assumption does not guarantee the existence of such a state. (For example, the strictly convex function e^{-x} on the real line does not have a minimum.)

The existence of at least one possible final equilibrium state of the closed composite thermodynamic system depicted in Fig. 5 is guaranteed by a condition that will now be stated. It will be assumed that the fundamental energy functions U_1 and

U_2 (restricted to the variables that appear in the vector x) are differentiable in the interior of their effective domains; these interior sets of equilibrium states will be denoted by E_1 and E_2 , respectively. For equilibrium states x_1 in E_1 and x_2 in E_2 , the gradient vectors $\nabla U_1(x_1)$ and $\nabla U_2(x_2)$ represent the values that can be assumed by some of the intensive parameters of the systems in the states x_1 and x_2 , and will be denoted by $P_1(x_1)$ and $P_2(x_2)$, respectively. Suppose that there exists an equilibrium state x in E_1 such that the state $x_t - x$ is in E_2 , and such that the gradient vector

$$\nabla U_t(x) = P_1(x) - P_2(x_t - x)$$

is precisely the zero vector. Suppose, in addition, that the set of vectors

$$\{P_1(y) - P_2(x_t - y) \mid y \in E_1\}$$

contains an open neighbourhood of the zero vector. Under these conditions, there exists at least one possible final equilibrium state of the composite thermodynamic system and in addition the set of all possible final equilibrium states is bounded. This follows from Theorem 15 and a result of convex analysis that has already been mentioned in Section 2.2: the minimum set of a closed proper convex function f defined on R^n is nonempty and bounded if and only if $0 \in \text{int}(\text{dom } f^*)$.

It is of interest to obtain a more satisfactory proof of the existence of possible final equilibrium states of closed composite thermodynamic systems. Here is a proof that does not use any differentiability assumptions and that establishes the existence of minimum points of total energy functions for most cases. Note that in many cases the effective domain of the total energy function U_t defined by Eq. (30) is bounded. Assume, for example, that all independent extensive parameters involved can only have nonnegative values. Then the total energy function U_t is a closed proper convex function whose effective domain is bounded: the vector x is an element of the effective domain of U_t only if $x \geq 0$ and $x \leq x_t$. (For vectors $x = (x_1, \dots, x_n)$ and $y = (y_1, \dots, y_n)$ in R^n , define $x \leq y$ if the ordinary inequality $x_i \leq y_i$ holds for all $i = 1, \dots, n$.) If the effective domain of the total energy function U_t defined by Eq. (30) is bounded, then this function has at least one minimum point. This follows from the following result.

THEOREM 31. *If f is a closed proper convex function defined on R^n and if $\text{dom } f$ is bounded, then there exists at least one minimum point of f .*

In order to prove this, denote the infimum of the numbers $f(x)$ as x ranges over R^n by $\inf f$, and choose a sequence of real numbers λ_n such that $\lambda_n > \lambda_{n+1}$ for all n and such that $\lambda_n \rightarrow \inf f$ as $n \rightarrow \infty$. Define the sets S_n by

$$S_n = \{x \in R^n \mid f(x) \leq \lambda_n\}.$$

The sets S_n are nonempty, closed (because f is closed and hence lower semicontinuous), and bounded (because $\text{dom } f$ is bounded). Hence the sets S_n are non-

empty compact subsets of R^n . Since, in addition, the sets S_n are decreasing (i.e., $S_n \supset S_{n+1}$ for all n), it follows that the intersection of the sets S_n is nonempty [9, p. 38]. Since this intersection coincides precisely with the set $\{x \in R^n \mid f(x) = \inf f\}$, it follows that the minimum set of f is nonempty. (Since f is a proper convex function, it follows in addition that $\inf f$ is finite.)

In addition to the question of the existence of minimum points of total energy functions of closed composite thermodynamic systems, one can also ask whether such minimum points are always unique. In other words, can equilibrium thermodynamics always uniquely predict a final equilibrium state found by a closed composite thermodynamic system? One might speak of a case of "thermodynamic uncertainty" when the set of possible final equilibrium states of a closed composite thermodynamic system (i.e., the minimum set $\partial U_i^*(0)$ of the total internal energy) contains more than one state.

A concrete example of thermodynamic uncertainty will now be described. Suppose that in the situation depicted in Fig. 5 the two thermodynamic systems are identical one-component chemical systems, for example, pure water. Then the fundamental energy functions U_1 and U_2 are both given by the same convex function $U(S, V, N)$, where S denotes the entropy, V the volume, and N the mole number of a system. Suppose that the separation between the two systems is diathermal, movable, and not permeable to water in any form. Suppose that after this composite thermodynamic system has been left to itself for a long time, a final equilibrium state is reached in which both systems contain water in significant amounts of precisely two phases: liquid and vapor. Then there exist different possible final equilibrium states with the same total entropy and internal energy, differing only in the fraction of vapor in the two subsystems. Hypothetically, these different possible final equilibrium states might be reached by transferring some entropy in a reversible way from one system through the separation to the other system; then, the fraction of vapor in the first system would be reduced and the fraction of vapor in the second system would be increased. After such a transfer of entropy through the separation between the systems, the total internal energy U_i and the total entropy would have precisely the same value as before the transfer. Hence in this case there is more than one state with the same total internal energy for the given value of the total entropy, so that this is a concrete example of what is called above "thermodynamic uncertainty": final equilibrium states of closed composite thermodynamic systems cannot always be uniquely predicted using only the minimum energy principle from equilibrium thermodynamics.

This example of an indeterminate energy minimization problem leads to the following more general discussion of the uniqueness of the possible final equilibrium states of closed composite thermodynamic systems. We shall use the formal definitions of thermodynamic stability and multiphase states that were given in Section 3. Reconsider the general closed composite thermodynamic system of Fig. 5, whose possible final equilibrium states x minimize the total internal energy function U_i defined by Eq. (30). Suppose that the set of possible final equilibrium states $\partial U_i^*(0)$ is nonempty. Let x be an arbitrary state in the set $\partial U_i^*(0)$. Then this state x

is the only possible final equilibrium state if either the state x is a thermodynamically stable equilibrium state of System 1, or if $x_i - x$ is a thermodynamically stable equilibrium state of System 2. In order to show this, assume for example that x is a thermodynamically stable equilibrium state of System 1. Then, as is easily seen, the function U_i defined by Eq. (30) is strictly convex on an open convex neighborhood of the state x , so x is the only minimum point of U_i . If, on the other hand, the states x and $x_i - x$ are both thermodynamically unstable equilibrium states, of Systems 1 and 2, respectively, then the set of possible final equilibrium states $\partial U_i^*(0)$ may contain more than one state x . Suppose, for example, that the two thermodynamic systems are identical (i.e., that they have the same fundamental energy functions) and that the states x and $x_i - x$ are distinct two-phase states, involving the same phase transition (cf. the example of the preceding paragraph). Then the states x and $x_i - x$ are both contained in one and the same line segment of length >0 , on which the fundamental energy function U of the two systems is flat. Hence for all states $\lambda x + (1 - \lambda)(x_i - x)$ such that $0 \leq \lambda \leq 1$, the total internal energy has the same value:

$$\begin{aligned} U_i(\lambda x + (1 - \lambda)(x_i - x)) \\ &= U(\lambda x + (1 - \lambda)(x_i - x)) + U(x_i - (\lambda x + (1 - \lambda)(x_i - x))) \\ &= \lambda U(x) + (1 - \lambda) U(x_i - x) + U(\lambda(x_i - x) + (1 - \lambda)x) \\ &= U(x) + U(x_i - x) = U_i(x). \end{aligned}$$

Hence if in this example the equilibrium state x is contained in the minimum set of the total energy U_i , then this minimum set contains a whole line segment of length >0 .

As has already been mentioned in Section 3, the surface between the distinct phases of a thermodynamic system is not explicitly taken into account in this paper. If such surfaces were taken into account, then possible final equilibrium states of closed composite thermodynamic systems might be unique even in the cases just treated [26]. The uniqueness of possible final equilibrium states of closed composite thermodynamic systems would follow rigorously in all situations involving more than one phase, if fundamental energy functions are not flat but ("slightly") strictly convex in open convex neighborhoods of multiphase states. Note that in this case, however, constructions such as the lever rule could not be applied strictly to determine the amounts of the different phases into which a system is split up in a multiphase state. It is clear that even if fundamental energy functions are not exactly flat but slightly strictly convex in open convex neighborhoods of multiphase states, then the phenomenon of thermodynamic uncertainty as described above would still occur, albeit only approximatively.

Using a symmetry argument, the problem of finding the final equilibrium states of a closed composite thermodynamic system can be given explicitly in the following special case. Suppose that the two thermodynamic systems of the situation depicted in Fig. 5 have the same fundamental energy function and suppose that the

independent extensive parameters for which the separation between the two systems is not permeable, have the same value in the two systems. Suppose in addition that the equilibrium state x of System 1 minimizes the total energy function U_t defined by Eq. (30), and that this state is thermodynamically stable, so it is the only minimum point of U_t . By symmetry, it follows that the function U_t will also assume its global minimum in the state $x_t - x$. By uniqueness, it follows that $x_t - x = x$, so an explicit expression for the unique minimum point of the total energy U_t is given by $x = x_t/2$. Hence both systems are thermodynamically stable in this final equilibrium state. Suppose, for example, that both systems in Fig. 5 consist of the same amount N of a one-component system, and that the separation between the system is a diathermal movable piston. The result just proved implies that in this example one can never find a final equilibrium state in which one of the parts of the composite thermodynamic system is thermodynamically stable, and in which the other part contains more than one phase.

There is a special entropy maximization problem that has been considered indeterminate by some authors: the problem of finding the final equilibrium state of a closed composite thermodynamic system consisting of two parts separated by a piston that is freely movable but "impermeable" to entropy, chemical components, etc. In [5, Appendix C] this problem with internal adiabatic constraints is investigated using the entropy representation. It is tempting to analyze this problem using the techniques provided by convex analysis to see if the minimum set of the total energy U_t (i.e., $\partial U_t^*(0)$) does indeed contain more than one state. However, the entropy representation analysis of [5, Appendix C] contains an error: this problem is as determinate as most other entropy maximization problems of equilibrium thermodynamics. This can easily be seen generally when the problem is analyzed from the point of view of the energy representation instead of the entropy representation. Alternatively, one can solve the problem for a particular thermodynamic system, e.g., blackbody radiation (see Eq. (17)): minimizing the total energy $U_t = bS_1^{4/3}V_1^{-1/3} + bS_2^{4/3}(V_t - V_1)^{-1/3}$ as a function of V_1 , at constant entropies S_1 and S_2 and at constant total volume $V_t = V_1 + V_2$ yields the unique solution $V_1 = S_1 V_t / (S_1 + S_2)$. (If $S_1 = S_2$, then this reduces to a special case of the symmetric solution $x = x_t/2$ obtained in the preceding paragraph.) The error of the treatment given in [5, Appendix C] seems to be that the variables U_1 , V_1 (and U_2 , V_2) are at the same time taken to be independent (entropy representation!) and related, via $dU_1 = -p_1 dV_1$ (and $dU_2 = -p_2 dV_2$). The fact that the analysis of [5, Appendix C] is erroneous has also been shown (using more elaborate reasoning) by Curzon and Leff [27].

This section will now be concluded with a general discussion of the problem of thermodynamically predicting the final equilibrium states of a closed composite system consisting of a thermodynamic system that is interacting with some large reservoirs. Suppose that a thermodynamic system with fundamental energy function U (defined on a Euclidean space R') can interact with n large reservoirs ($n < t$), with constant intensive parameters given by a vector $P_r = (P_{1r}, \dots, P_{nr}) \in R''$. Then the possible final equilibrium states of the system minimize the total internal energy.

In the standard textbooks this condition is translated into a minimization problem for transformed fundamental functions (see, e.g., [5, Chapter 5]). More generally, the possible final equilibrium states of the system can be found by minimizing the *nonflow availability function* A , which is defined (using an inner product) by

$$A(x) = U(x) - (P_r, x) \quad (x \in R^n). \quad (32)$$

Even when initially the intensive parameters of the system are not equal to the intensive parameters of the reservoirs, the possible final equilibrium states of the system can be found by minimizing the availability function A . Hence the minimization of such nonflow availability functions is more generally applicable than the minimization of transformed fundamental functions. In addition, since nonflow availability functions differ from fundamental energy functions only by a linear term, their mathematical form is simpler than that of transformed fundamental functions. (These functions are called availability functions because the difference of an availability function in two states gives the maximum work that can be performed in a process in which the system is transformed from one state to the other. The function given in Eq. (32) is referred to as a "nonflow" availability function because there are also "steady-flow availability functions," which differ from enthalpies by a linear term; see, e.g., [28].) By the general minimization theory summarized in Section 2.2, the minimum set of the availability function A can be mathematically characterized as the subdifferential of the convex conjugate function of A at 0: $\partial A^*(0)$. If there exists only one such minimum point, then this state can in principle be calculated by differentiating the convex conjugate of the availability function A at 0: $\nabla A^*(0)$. Suppose that the fundamental energy function U is differentiable in the interior of its effective domain. For an arbitrary equilibrium state x in the interior of the effective domain of the fundamental energy function U , the vector components of the gradient vector $\nabla U(x)$ are simply the intensive parameters of the system in the state x : $\nabla U(x) = P(x)$. It follows that

$$\nabla A(x) = \nabla U(x) - P_r = P(x) - P_r.$$

Since U is convex, A is also convex. (Furthermore, the closedness of U implies the closedness of A .) Mathematically, the problem of the existence of minimum points of nonflow availability functions is the same as the problem of the attainment of the infimum in the definition of transformed fundamental functions (see Eq. (20)). Using the equivalence of the assertions stated in (6) (see Section 2.2), it can be concluded that if the system has an equilibrium state x such that $P(x) = P_r$, then the availability function A has a global minimum which is attained in x . In addition, using reasoning similar to that used above, if this state is thermodynamically stable in the sense defined in Section 3, then this state is the unique minimum point of the availability function (32). A minimum point of the availability function A defined by Eq. (32) is not unique if the vector P_r coincides precisely with the gradient of U at a flat part of U (cf. the discussion following Eq. (21)), i.e., if the system is split up into distinct phases. It seems that the existence of minimum points x of availability

functions satisfying $P(x) = P$, does not follow generally from the stated general mathematical properties of the fundamental energy functions of equilibrium thermodynamics.

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