

Metric geometry of equilibrium thermodynamics

F. Weinhold*

Department of Chemistry, Stanford University, Stanford, California 94305
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It is shown that the principal empirical laws of equilibrium thermodynamics can be brought into correspondence with the mathematical axioms of an abstract metric space. This formal correspondence permits one to associate with the thermodynamic formalism a geometrical aspect, with intrinsic metric structure, which is distinct from that arising from graphical representations of equilibrium surfaces in phase space.

I. INTRODUCTION

It has been known, particularly since the early works of Gibbs,¹ that the analysis of systems in thermodynamic equilibrium can be considerably facilitated with the help of graphical and geometrical methods. Gibbs pointed out the advantage of geometrically representing thermodynamic properties of simple fluids by means of surfaces in "Gibbs space"²—rectangular coordinates labeled by the internal energy, entropy, and volume of the system. The geometrical analysis of equilibrium surfaces in Gibbs space, or other related phase spaces, continues to play an important role in more modern aspects of thermodynamic research.³

While thermodynamic systems thus appear to have an important geometric aspect, it has been generally recognized that the "geometry" of thermodynamic phase spaces lacks an intrinsic *metric* structure.⁴ This circumstance results essentially from the arbitrariness of units which might be chosen for the various coordinate axes, and from the rather arbitrary selection of the Cartesian axes themselves from among a wide variety of possible coordinate systems. For this reason, distances, angles, areas, "direction," and other natural geometrical concepts do not generally have an intrinsic thermodynamic significance in such spaces.

In the present paper we wish to call attention to the existence of another, quite different form of geometry in the thermodynamic formalism. It will be found possible to construct, within the confines of this formalism, a linear vector space which, although of an abstract nature, possesses a full metric structure and is therefore isomorphic to an ordinary Euclidean space of corresponding dimensionality. The abstract metric structure derives rather directly from general thermodynamic principles—empirical "laws" of universal experience—which underlie the thermodynamic formalism. As such, the metric geometry may offer the possibility of an alternative representation of this formalism (or selected aspects thereof) with certain novel features.

II. SYNOPSIS OF THE EMPIRICAL BASIS FOR EQUILIBRIUM THERMODYNAMICS

In order to identify clearly the origins of the abstract metric structure, we first briefly summarize the empirical observations which underlie equilibrium thermodynamics, so as to bring these observations into a convenient form for the later analysis.

A. Fundamental equation and laws of thermodynamics

Following generally the Callen⁵–Tisza⁶ ("neo-Gibbsian"⁷) treatment, particularly in its emphasis on individual thermodynamic *states* rather than *processes* as primary elements of the formalism,⁸ we consider the elementary thermodynamics of a simple system such as a fluid in the absence of external fields, surface effects, etc., though the treatment will not preclude certain standard extensions to more complex systems. At the outset, nonthermal concepts such as pressure, volume, etc., are regarded as established, and we further assume that such properties as temperature, internal energy, and entropy have been introduced in some orderly manner⁹ and are understood to have definite operational significance.

It is observed that an equilibrium state can be completely characterized, for thermodynamic purposes, in terms of only a small, determinate number r (fixed by the Gibbs phase rule¹⁰) of independent state properties. Following Gibbs¹¹ (in the "energy representation"¹²), we are then led to associate with the system a *fundamental equation* of the form

$$U = U(X_1, X_2, \dots, X_r, X_{r+1}), \quad (1a)$$

in which internal energy U is expressed as a function of extensive state properties X_i . Although these latter are commonly chosen to be entropy S , volume V , mole numbers N_i , etc., we can more generally regard each X_i as some arbitrary linear combination of the reference extensivities S, V, N_i, \dots ¹³ Since the overall scale of the system is not ascribed thermodynamic significance, one argument of the fundamental equation, say, X_{r+1} (usually total mass or volume), is to be held fixed as the "scale factor"¹⁴ for the system, and can then be suppressed from the argument list,

$$U = U(X_1, X_2, \dots, X_r). \quad (1b)$$

The functional relationship which connects the independent extensive variables in Eq. (1) is moreover observed to be sufficiently well behaved to permit the application of the partial differential calculus in the familiar manner. Thus, with each extensity X_i one can associate the corresponding *field*¹⁵ variable R_i ,

$$R_i \equiv \partial U / \partial X_i, \quad (2)$$

which is said to be *conjugate* to X_i . The fields R_i are themselves observed to be differentiable functions of the extensivities, and the *first law*—the observation that in-

ternal energy is a conserved function of state, and thus has an exact differential—is usually expressed through the cross-differentiation identity¹⁶

$$\left. \frac{\partial R_i}{\partial X_j} \right|_{\xi} = \left. \frac{\partial R_j}{\partial X_i} \right|_{\xi}, \quad (3)$$

involving such field derivatives. The subscript vector ξ denotes that the partial derivative is to be evaluated at the point ξ in Gibbs space, e.g., at the point where each X_i assumes the numerical value ξ_i corresponding to the particular equilibrium state in question.

Perhaps the most characteristic observation concerning equilibrium states is the extremum principle summarized in the *second law*, the observation that energy is minimized at constant entropy (or, equally, that entropy is maximized at constant energy¹⁷) in an isolated equilibrium state. This observation can be expressed through a convexity relation of the form¹⁸

$$U(X_i) \leq \frac{1}{2}[U(X_i + \delta X_i) + U(X_i - \delta X_i)] \text{ at } \xi, \quad (4a)$$

for arbitrary infinitesimal variations δX_i . Alternatively, the minimum property of U can be expressed through the usual second-derivative condition¹⁹

$$\left. \frac{\partial^2 U}{\partial X_i^2} \right|_{\xi} = \left. \frac{\partial R_i}{\partial X_i} \right|_{\xi} \geq 0, \quad (4b)$$

expressing the upward curvature of the energy function with respect to small displacements about the isolated equilibrium state. Inequalities (4) essentially summarize Le Châtelier's principle concerning the restorative tendency (e.g., *stability*) of thermodynamic equilibrium. Since the X_i 's denote arbitrary linear combinations of the chosen set of reference extensivities, it is necessary that conditions (3) and (4) be understood to hold for each value of the index i , and for every possible manner of choosing the X_i 's.

[We do not include the "third law of thermodynamics" (Nernst postulate²⁰) in this brief synopsis. The third law occupies a quite different position in the traditional thermodynamic formalism than do the first and second laws,²¹ and apparently plays only a rather indirect role in the construction of the metric geometry.²²]

B. Scope of a thermodynamic description

Although the fundamental equation (1) materially simplifies the thermodynamic analysis and allows for easy expression of the first and second laws, it is apparent that this function contains more information than is strictly necessary for a thermodynamic description of a given equilibrium state. Indeed, the full functional form of the fundamental equation is seldom, if ever, known in practice.²³ To properly characterize the basis of the thermodynamic analysis, we should therefore distinguish features of the fundamental equation which are essential from those which are inessential to the thermodynamic description of a given state. In effect, this delineation of the natural scope of a thermodynamic description will indicate an important simplifying feature of the formalism.

Following Gibbs,²⁴ we may regard the stability condition (4) as a characteristic *criterion* for a state of ther-

modynamic equilibrium. As such, it provides a form of definition of the equilibrium state, and thus of the characteristic scope of its thermodynamic description. In particular, we can observe that conditions (3) and (4) involve at most the *first* derivatives of field quantities R_i . It is therefore appropriate to restrict attention to those properties which refer only to this limited feature of the field functions R_i .²⁵ Conversely, for the usual class of thermodynamic properties of interest, one needs to consider only a rather simple aspect of the functional behavior of these field functions, namely, their lowest-order derivative. For this reason, the space of field functions has, for thermodynamic purposes, a very much simpler structure than might otherwise be supposed.

For example, one might choose to introduce some new set of field variables \tilde{R}_i which are arbitrary functions of the reference fields R_i ,

$$\tilde{R}_i = \tilde{R}_i(R_1, R_2, \dots, R_r), \quad i = 1, 2, \dots, r \quad (5a)$$

subject only to the usual condition of independence

$$\frac{\partial(\tilde{R}_1, \tilde{R}_2, \dots, \tilde{R}_r)}{\partial(R_1, R_2, \dots, R_r)} \neq 0 \text{ at } \xi. \quad (5b)$$

But if R and \tilde{R} are two "different" field variables whose first differentials coincide at the point ξ ,

$$dR(\xi) = d\tilde{R}(\xi), \quad (6a)$$

then they could be used interchangeably for calculating the properties of the state ξ , and need not be further distinguished,²⁶

$$R \text{ "=" } \tilde{R} \text{ for state } \xi. \quad (6b)$$

More generally, the differential of any permissible thermodynamic field quantity \tilde{R}_i can be expressed in the neighborhood of equilibrium state ξ as a simple *linear* combination of the differentials dR_j of some chosen reference set,

$$d\tilde{R}_i = \sum_{j=1}^r a_{ij} dR_j, \quad (7)$$

where

$$a_{ij} \equiv \left. \frac{\partial \tilde{R}_i}{\partial R_j} \right|_{\xi}. \quad (8)$$

Equation (7) allows one to associate with each permissible field variable \tilde{R}_i a coefficient vector \mathbf{a}_i ,

$$\mathbf{a}_i \equiv \begin{pmatrix} a_{i1} \\ a_{i2} \\ \vdots \\ a_{ir} \end{pmatrix}, \quad (9)$$

which can be used to *label* the field (for thermodynamic purposes)

$$R_{\mathbf{a}_i} = \tilde{R}_i \quad (10)$$

in a unique manner; note that the label \mathbf{a}_i depends generally on the particular equilibrium state ξ under discussion, as well as on the specific choice of reference fields R_i . If λ and μ are arbitrary scalars, it then fol-

lows that

$$dR_{\lambda a_i + \mu a_j} = \lambda dR_{a_i} + \mu dR_{a_j}, \tag{11}$$

which expresses directly the linear character of the field space in the domain of thermodynamic interest, e.g., in the immediate neighborhood of the equilibrium state ξ .

As a further consequence of this linearity, the general notion of *conjugacy* between fields and extensities can be retained even for field variables introduced in a quite arbitrary manner. For if we suppose that differentials of the old and new fields are connected as in Eq. (7) by a set of linear equations whose coefficients are elements of a matrix \mathbf{A} ,

$$(\mathbf{A})_{ij} = a_{ij}, \tag{12}$$

then the *inverse transpose* matrix \mathbf{A}^{-t} [which must exist in view of Eq. (5b)] will have elements, denoted \bar{a}_{ij} ,

$$(\mathbf{A}^{-t})_{ij} \equiv (\mathbf{A}^{-1})_{ji} \equiv \bar{a}_{ij}, \tag{13}$$

which will serve to define the appropriate set of conjugate extensities \bar{X}_i through the equation

$$\bar{X}_i = \sum_{j=1}^r \bar{a}_{ij} X_j. \tag{14}$$

Indeed, one can show without difficulty that

$$\frac{\partial U}{\partial \bar{X}_i} = \sum_{j=1}^r a_{ij} R_j, \tag{15}$$

and hence that²⁶

$$\bar{R}_i \equiv \partial U / \partial \bar{X}_i \tag{16}$$

for thermodynamic purposes, since the differentials of these two functions coincide in state ξ .

C. Summary

In summary, the key empirical observations which a formal theory of equilibrium thermodynamics must undertake to incorporate, and draw inferences from, include the following.

(a) The observation that properties of an equilibrium system may be associated with low-order derivatives (specifically, the r independent field differentials dR_i) of a mathematical function U which (i) involves only a small determinate number r of independent state variables, and (ii) is sufficiently smooth to permit application of the partial differential calculus in the usual manner.

(b) The *first law*, e.g., the observation that the internal energy function U satisfies the requirement for an exact differential,

$$\frac{\partial R_i}{\partial X_j} \Big|_{\xi} = \frac{\partial R_j}{\partial X_i} \Big|_{\xi}.$$

(c) The *second law*, e.g., the observation that internal energy is minimized in an isolated equilibrium state²⁷

$$\frac{\partial R_i}{\partial X_i} \Big|_{\xi} \geq 0.$$

III. CONSTRUCTION OF A THERMODYNAMIC METRIC

It is well known that abstract mathematical objects can sometimes be ascribed an abstract metric character, i.e., can be associated with elements of an abstract metric space in a manner which allows these objects to be manipulated like ordinary vectors in an ordinary Euclidean space. A familiar example in quantum mechanics is the abstract metric *Hilbert space*, which permits wavefunctions to be dealt with as "state vectors" having many properties in common with ordinary Euclidean vectors. We now inquire whether such an association can be found within the formalism of equilibrium thermodynamics.

The key mathematical requirement for an abstract metric space \mathfrak{M}_r of dimension r is that it should be possible, for any pair of "vectors" $|\mathcal{R}_i\rangle, |\mathcal{R}_j\rangle$, to form a *scalar product* $\langle \mathcal{R}_i | \mathcal{R}_j \rangle$ having the properties²⁸

- (a') $\langle \mathcal{R}_i | \lambda \mathcal{R}_j + \mu \mathcal{R}_k \rangle = \lambda \langle \mathcal{R}_i | \mathcal{R}_j \rangle + \mu \langle \mathcal{R}_i | \mathcal{R}_k \rangle$,
- (b') $\langle \mathcal{R}_i | \mathcal{R}_j \rangle = \langle \mathcal{R}_j | \mathcal{R}_i \rangle$,
- (c') $\langle \mathcal{R}_i | \mathcal{R}_i \rangle \geq 0$ (equality only if $|\mathcal{R}_i\rangle = 0$).

In particular, the distributive axiom (a') requires that it should always be meaningful to form the vector

$$|\lambda \mathcal{R}_i + \mu \mathcal{R}_j\rangle = \lambda |\mathcal{R}_i\rangle + \mu |\mathcal{R}_j\rangle \tag{17}$$

from any pair of vectors $|\mathcal{R}_i\rangle, |\mathcal{R}_j\rangle$ and real scalars λ, μ . An abstract space having properties (a')–(c') is mathematically isomorphic to a corresponding Euclidean space of r dimensions.²⁹

It is now possible to establish the essential equivalence of the empirical laws (a)–(c) (Sec. IIC) and the mathematical axioms (a')–(c') by formally associating with each field differential dR_i an abstract vector,

$$dR_i \leftrightarrow |\mathcal{R}_i\rangle, \tag{18}$$

with the scalar product

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle \equiv \frac{\partial R_i}{\partial X_j} \Big|_{\xi}. \tag{19}$$

In this equation, X_j represents the extensive variable conjugate to R_j in the sense of Eq. (2) (for a reference field) or in the generalized sense of Eq. (16) (for an arbitrary field).

With the identification, Eq. (19), of the scalar product, it can be recognized that observation (a), which led to Eq. (11), will cause Eq. (17) and the distributive axiom (a') to hold. Moreover, the correspondence between (b) and (b') can be readily seen, as can the general correspondence between (c) and (c'). In this latter case, however, an additional comment is necessary with respect to the non-negativity axiom (c'), since it has not been made explicit that the parenthesized condition $\langle \mathcal{R}_i | \mathcal{R}_i \rangle = 0$ to imply $|\mathcal{R}_i\rangle = 0$ has a proper counterpart in the thermodynamic observations (a)–(c), e.g., that $\partial R_i / \partial X_i = 0$ implies $dR_i = 0$.

To see that this is the case, suppose on the contrary that $\partial R_i / \partial X_i = 0$ for some *nonzero* field differential dR_i , which can then be taken as one of the r independent field

differentials to describe the system. The usual condition of independence of these field differentials, the nonvanishing of the Jacobian determinant,

$$\frac{\partial(R_1, R_2, \dots, R_r)}{\partial(X_1, X_2, \dots, X_r)} = \det \left| \frac{\partial R_i}{\partial X_j} \right| \neq 0, \quad (20)$$

is, however, incompatible with the assumption

$$\partial R_i / \partial X_i = 0, \quad (21)$$

since it is well known from general matrix theory that a positive semidefinite matrix³⁰ with any vanishing diagonal element is necessarily singular.³¹ Therefore, equality in Eq. (21), except for the trivial case $dR_i = 0$, is in effect incompatible with the Gibbs phase rule, inasmuch as it would imply the existence of some *new* field variables in which thermodynamic equations of state could be written with fewer than r variables. Thus, the abstract axiom (c') must also be fulfilled by the thermodynamic observations (a)–(c) in respect to the special case $\langle R_i | R_i \rangle = 0$,³² and the formal association of the basic empirical observations of equilibrium thermodynamics with the mathematical axioms of an abstract geometry is thereby complete. Of course, the number r of independent thermodynamic field differentials is finally to be associated with the dimensionality of the metric space \mathcal{M}_r , as our notation has anticipated.

IV. CONCLUSION

The empirical laws of equilibrium thermodynamics have been shown to reflect an interesting underlying structure of a geometric nature. The close connection between these thermodynamic laws and the axioms of an abstract metric space suggests that the latter mathematical structure may allow for an alternative representation of the thermodynamic formalism with certain possible advantages over the traditional one. Such a geometric representation would naturally invite use of vector- and matrix-algebraic methods in place of the partial differential equations of the usual approach. It is intended that various aspects of such a complementary representation of equilibrium thermodynamics will be investigated in subsequent papers.

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*Camille and Henry Dreyfus Foundation Fellow.

¹J. W. Gibbs, *Collected Works* (Longmans, Green, and Co., New York, 1928), Vol. I, pp. 1–54.

²L. Tisza, *Ann. Phys. (N.Y.)* **13**, 1 (1961).

³See, e.g., R. B. Griffiths, *Phys. Rev. Lett.* **24**, 715 (1970); J. T. Barts, *J. Chem. Phys.* **59**, 5423 (1973); T. S. Chang, A. Hankey, and H. E. Stanley, *Phys. Rev. B* **8**, 346 (1973).

⁴L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, 1966), pp. 235–241; E. K. Riedel, *Phys. Rev. Lett.* **28**, 675 (1972); cf. also Gibbs, Ref. 1, p. 34.

⁵H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

⁶See Refs. 2 and 4.

⁷Tisza, Ref. 4, p. 49.

⁸Tisza, Ref. 4, p. 40; Callen, Ref. 5, p. viii.

⁹P. T. Landsberg, *Thermodynamics, With Quantum Statistical Illustrations* (Interscience, New York, 1961), pp. 53ff.; Callen, Ref. 5, pp. 15ff.

¹⁰While the phase rule is sometimes “derived” in elementary texts, its deduction rests in an essential way on the *empirical* observation that exactly two variables suffice to characterize the simplest (single-phase, single-component) fluid systems.

¹¹Ref. 1, pp. 85–89.

¹²Ref. 5, p. 36; Tisza, Ref. 4, p. 42.

¹³This more general definition of the X_i 's, which is suggested immediately by the metric structure, may also be of practical importance in the investigation of real physical systems. For example, when heat is added to a fixed quantity of fluid, it may not be experimentally feasible to confine the system at constant volume, and the variable which is practically at the investigator's disposal is then some combination of S and V . See, J. S. Rowlinson, *Liquids and Liquid Mixtures* (Academic, New York, 1959), pp. 40ff.

¹⁴Tisza, Ref. 4, pp. 45 and 116.

¹⁵R. B. Griffiths and J. C. Wheeler, *Phys. Rev. A* **2**, 1047 (1970). The “fields” are essentially those intensive variables which, at equilibrium, assume the same numerical value in every portion of the system. Because the scale factor X_{r+1} is not necessarily total volume, we prefer to retain a more traditional nomenclature (instead of the Griffiths–Wheeler term, “densities”) for the extensive variables X_i .

¹⁶See, e.g., H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, 2nd edition (Van Nostrand, New York, 1956), pp. 8–12.

¹⁷See, e.g., Ref. 5, pp. 85–90. Note that it is the *existence* of an extremum principle, not its sense (e.g., whether maximum or minimum), which allows for the metric structure so that the existence of such a structure is not affected by “negative temperature” states as discussed by N. F. Ramsey, *Phys. Rev.* **103**, 20 (1956).

¹⁸See, e.g., M. E. Fisher, *Rept. Progr. Phys.* **30**, 615 (1967); H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University, New York, 1971), pp. 28ff.

¹⁹G. H. Hardy, J. E. Littlewood, and G. Polya, *Inequalities* (Cambridge University, Cambridge, 1967), pp. 91ff.

²⁰Tisza, Ref. 4, pp. 92–96; J. Wilks, *The Third Law of Thermodynamics* (Oxford University, London, 1961).

²¹See, e.g., Ref. 5, p. 27.

²²It has been recognized [see, e.g., R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University, New York, 1956), pp. 223–229] that the third law is expressed most generally as a “principle of unattainability of the absolute zero.” In this form, the third law does serve to remove certain potential difficulties in the metric formalism connected with the special limit $T=0$; see below, especially Ref. 32. (Thanks are due an anonymous referee for remarking that the the third law must play some role in defining a satisfactory metric.)

²³An exception is the ideal gas; see Ref. 1, pp. 150ff., or Ref. 5, pp. 51ff.

²⁴Ref. 1, pp. 56ff.

²⁵For example, one might investigate third or higher mixed partial derivatives of the energy function, but such “properties” (it being assumed the derivatives exist) are in general not subject to any special consequences of the first or second laws of thermodynamics, which are expressible in terms of first-order field derivatives alone. Such higher derivatives thus fall outside the class of properties, or *responses* (cf. H. E. Stanley, Ref. 18, pp. 25ff.), which are characteristic of a thermodynamic description. This distinction (and restriction) might be made explicit by referring to the “linear regime” in thermodynamics; only properties associated with

the linear regime, i. e., with *first* differentials of fields or extensities, will play a direct role in the thermodynamic geometry.

²⁶Equality sign in quotes, denoting a kind of thermodynamic equivalence, thus refers strictly to only the equality of first differentials at the point ξ .

²⁷In terms of a general field \bar{R}_i and its conjugate extensity \bar{X}_i as expressed in Eqs. (7) and (14), respectively, condition (c) becomes

$$\frac{\partial \bar{R}_i}{\partial \bar{X}_i} = \sum_{j,k=1}^r \frac{\partial \bar{R}_i}{\partial R_j} \frac{\partial R_j}{\partial X_k} \frac{\partial X_k}{\partial \bar{X}_i} = \sum_{j,k=1}^r a_{ij} \frac{\partial R_j}{\partial X_k} a_{ik} \geq 0,$$

which may be written in the form

$$a_i^t \mathbf{G} a_i \geq 0,$$

where

$$(\mathbf{G})_{ij} \equiv \partial R_i / \partial X_j.$$

Since the coefficient vector a_i is completely arbitrary, \mathbf{G} is necessarily a positive semidefinite matrix, which may be considered an alternative statement of condition (c).

²⁸P. Dennery and A. Krzywicki, *Mathematics for Physicists* (Harper and Row, New York, 1967), pp. 109–111; G. E.

Shilov, *An Introduction to the Theory of Linear Spaces* (Prentice Hall, Englewood Cliffs, NJ, 1961), pp. 135ff. We take \mathfrak{M}_r to be real.

²⁹Shilov, Ref. 28, pp. 143 and 144.

³⁰That the matrix whose elements are $\partial R_j / \partial X_j$ must be positive semidefinite was shown in Ref. 27.

³¹This follows directly from a well known theorem of Frobenius; see, e.g., L. Mirsky, *An Introduction to Linear Algebra* (Oxford University, New York, 1955), pp. 400ff.

³²The reader may remark that interesting special behavior is possible in the limit of collapse to lower dimensionality, e.g., at the “boundary” between \mathfrak{M}_r and \mathfrak{M}_{r-1} , where, for example, a differential dR_i which is not identically zero in \mathfrak{M}_r could nevertheless approach the limit $\partial R_i / \partial X_i = 0$. In view of the Gibbs phase rule, this “boundary” corresponds thermodynamically to the incipient formation of a new phase, e.g., to a critical point.

The geometric formulation might also appear to break down at the absolute zero of temperature (since T enters the expressions for several scalar products, and norms of some vectors may thereby appear to vanish or diverge at absolute zero), but the necessity to geometrically characterize this special limit is evidently obviated by the “principle of unattainability of the absolute zero,” Ref. 22.