Metric geometry of equilibrium thermodynamics

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(Received 5 August 1974)

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, 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"—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.

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. 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 Callen-Tisza ("neo-Gibbsian") treatment, particularly in its emphasis on individual thermodynamic states rather than processes as primary elements of the formalism, 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 manner 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 \( \nu \) (fixed by the Gibbs phase rule\(^{10} \)) of independent state properties. Following Gibbs\(^{11} \) (in the "energy representation"\(^{12} \)), we are then led to associate with the system a fundamental equation of the form

\[
U = U(X_1, X_2, \ldots, X_r, X_{\nu-1}),
\]

(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 extensities \( S, V, N_i, \ldots \)^{11} Since the overall scale of the system is not ascribed thermodynamic significance, one argument of the fundamental equation, say, \( X_{\nu-1} \) (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,

\[
U = U(X_1, X_2, \ldots, X_r).
\]

(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 \( R_i \),

\[
R_i = \frac{\partial U}{\partial X_i},
\]

(2)

which is said to be conjugate to \( X_i \). The fields \( R_i \) are themselves observed to be differentiable functions of the extensities, 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 identity

$$\frac{\partial R_i}{\partial X_j} = \frac{\partial R_i}{\partial X_k} \frac{\partial X_k}{\partial X_j},$$

(3)

involving such field derivatives. The subscript vector
$\xi$ denotes that the partial derivative is to be evaluated
at the point $\xi$ in Gibbs space, e.g., at the point where
each $X_i$ assumes the numerical value $\xi_i$ 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 en-
tropy is maximized at constant energy) in an isolated
equilibrium state. This observation can be expressed
through a convexity relation of the form

$$U(X) = \frac{1}{2}(U(X_1 + \Delta X_j) + U(X_1 - \Delta X_j))$$

at $\xi$, (4a)

for arbitrary infinitesimal variations $\Delta X_i$. Alterna-
tively, the minimum property of $U$ can be expressed
through the usual second-derivative condition

$$\frac{\partial^2 U}{\partial X_i^2} \geq 0,$$

(4b)

expressing the upward curvature of the energy function
with respect to small displacements about the isolated
equilibrium state. Inequalities (4) essentially sum-
marize Le Chatelier'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 extents, 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 postulate$^{26}$) in this brief synopsis. The third
law occupies a quite different position in the traditional
thermodynamic formalism than do the first and second
laws, 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 sim-
plifies 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 formal-
ism.

Following Gibbs,$^{24}$ we may regard the stability condi-
tion (4) as a characteristic criterion for a state of ther-

dynamic 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 $R_i$. 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 $R_i$,

$$\tilde{R}_i = \tilde{R}_i(R_{i1}, R_{i2}, \ldots, R_{ir}), \quad i = 1, 2, \ldots, r$$

(5a)

subject only to the usual condition of independence

$$\frac{\partial \tilde{R}_i}{\partial R_{i1}} \neq 0$$

at $\xi$. (5b)

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

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

(6a)

then they could be used interchangeably for calculating
the properties of the state $\xi$, and need not be further
distinguished.$^{26}$

$R \sim \tilde{R}$ for state $\xi$.

(6b)

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

$$d\tilde{R}_i = \sum_{i=1}^n a_{ij} dR_j,$$

(7)

where

$$a_{ij} = \frac{\partial \tilde{R}_i}{\partial R_j}(\xi).$$

(8)

Equation (7) allows one to associate with each permis-
sible field variable $\tilde{R}_i$ a coefficient vector $a_i$,

$$a_i = \begin{pmatrix}
    a_{i1} \\
    a_{i2} \\
    \vdots \\
    a_{ir}
\end{pmatrix},$$

(9)

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

$$R_{i1} = \tilde{R}_i,$$

(10)

in a unique manner; note that the label $a_1$ depends
generally on the particular equilibrium state $\xi$ under
discussion, as well as on the specific choice of reference
fields $R_i$. If $\lambda$ and $\mu$ are arbitrary scalars, it then fol-
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 \( \mathcal{M} \), of dimension \( r \) that it should be possible, for any pair of "vectors" \( |\alpha_i\rangle \) and \( |\beta_i\rangle \), to form a scalar product \( \langle \alpha_i | \beta_i \rangle \) having the properties\(^{26}\)

\[
\begin{align*}
(a') & \quad \langle \alpha_i | \lambda \beta_j + \mu \beta_j \rangle = \lambda \langle \alpha_i | \beta_j \rangle + \mu \langle \alpha_i | \beta_j \rangle, \\
(b') & \quad \langle \alpha_i | \beta_j \rangle = \langle \beta_j | \alpha_i \rangle, \\
(c') & \quad \langle \alpha_i | \beta_i \rangle \geq 0 \quad \text{for equality only if} \quad |\beta_i\rangle = 0.
\end{align*}
\]

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

\[
|\lambda \beta_i + \mu \beta_j\rangle = |\lambda |\beta_i\rangle + \mu |\beta_j\rangle
\]

from any pair of vectors \( |\alpha_i\rangle \), \( |\beta_i\rangle \) and real scalars \( \lambda \), \( \mu \). An abstract space having properties (a')-(c') is mathematically isomorphic to a corresponding Euclidean space of \( r \) dimensions.\(^{26}\)

It is now possible to establish the essential equivalence of the empirical laws (a)-(c) (Sec. II.C) and the mathematical axioms (a')-(c') by formally associating with each field differential \( dR_i \) an abstract vector, \( dR_i \equiv |\beta_i\rangle \),\(^{18}\)

\[
\begin{align*}
\langle \alpha_i | \beta_i \rangle & \equiv \langle \alpha_i | \beta_i \rangle \\
\frac{\partial R_i}{\partial X_i} & \equiv \frac{\partial R_i}{\partial X_i}.
\end{align*}
\]

In this equation, \( X_i \) represents the extensive variable conjugate to \( R_i \) 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 \( \langle \beta_i | \alpha_i \rangle = 0 \) to imply \( |\beta_i\rangle = 0 \) 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 this field, the nonvanishing of the Jacobian determinant,
\[ \frac{\partial (R_1, R_2, \ldots, R_n)}{\partial (X_1, X_2, \ldots, X_n)} = \text{det} \left[ \frac{\partial R_i}{\partial X_j} \right] \neq 0, \]
(20)
is, however, incompatible with the assumption
\[ \frac{\partial R_i}{\partial X_j} = 0, \]
(21)since it is well known from general matrix theory that a positive semidefinite matrix with any vanishing diagonal element is necessarily singular. Therefore, equality in Eq. (21), except for the trivial case \( \frac{\partial R_i}{\partial X_j} = 0 \), 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 \( \frac{\partial R_i}{\partial X_j} = 0 \) 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 \( \mathbb{R}^r \), 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.

ACKNOWLEDGMENTS

I have appreciated the opportunity to discuss various aspects of this work with H. C. Andersen, M. E. Fisher, R. B. Griffiths, M. S. Hudson, and F. O. Koenig. The financial support of a Dreyfus Foundation Teacher–Scholar Grant is gratefully acknowledged.

*Camille and Henry Dreyfus Foundation Fellow.


6See Refs. 2 and 4. 

7Tisza, Ref. 4, p. 49.

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


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 \( \delta T \) and \( V \). See, J. S. Rowlinson, Liquids and Liquid Mixtures (Academic, New York, 1960), pp. 40ff.

14Tisza, Ref. 4, p. 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 \( X_{ri} \) is not necessarily total volume, we prefer to retain a more traditional nomenclature (instead of the Griffiths–Wheeler term, "densities") for the extensive variables \( \Xi \).


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. 102, 20 (1956).


21See, e.g., Ref. 5, pp. 27.

22It has been recognized (see, e.g., R. Fowler and E. A. Guggenheim, Statistical Thermodynamics (Cambridge University, New York, 1958), 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 \( T \to 0 \); 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.

Equality sign in quotes, denoting a kind of thermodynamic equivalence, thus refers strictly to only the equality of first differentials at the point \( t \).

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

\[
\frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_j} = \sum_{i,j,k,l} \frac{\partial \mathbf{R}_l}{\partial \mathbf{X}_j} \frac{\partial \mathbf{R}_j}{\partial \mathbf{X}_k} \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_l} = \sum_{i,j,k,l} a_{ij} \frac{\partial \mathbf{R}_l}{\partial \mathbf{X}_j} \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_l} \geq 0,
\]

which may be written in the form

\[
\mathbf{G} a_i = 0,
\]

where

\[
(\mathbf{G})_{ij} = \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_j}.
\]

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).


Shilov, Ref. 28, pp. 143 and 144.

That the matrix whose elements are \( \frac{\partial \mathbf{R}_i}{\partial \mathbf{X}_j} \) must be positive semidefinite was shown in Ref. 27.

This 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. 406 ff.

The reader may remark that interesting special behavior is possible in the limit of collapse to lower dimensionality, e.g., at the “boundary” between \( \pi_\alpha \) and \( \pi_{\alpha_i} \), where, for example, a differential \( d\mathbf{R}_i \) which is not identical zero in \( \pi_\alpha \) could nevertheless approach the limit \( d\mathbf{R}_i/d\mathbf{X}_i = 0 \). 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 evident by the “principle of unattainability of the absolute zero,” Ref. 22.