Thermodynamics and geometry

In the fulfillment of a goal envisioned by Gibbs, the laws of thermodynamics have been written in the form of a Euclidian metric geometry; its formulas can be read off from simple diagrams.

Frank Weinhold

It is perhaps appropriate that, in a year marking the 100th anniversary of his landmark paper in thermodynamics, new developments should call fresh attention to the special beauty and profundity of the work of J. Willard Gibbs. Recent work[1] has proved the possibility of constructing a new representation of equilibrium thermodynamics, one that is couched in a mathematical language—an intrinsically geometrical structure—quite different from that generally employed.

This concept of the geometrization of thermodynamics emerges rather directly from Gibbs's point of view, which is summarized in the Box on the following page. In the traditional textbook viewpoint, which had originated with Sadi Carnot and Lord Kelvin, these ideas are recognizable only dimly at best. It is remarkable that Gibbs arrived at a formulation that lends itself so well to transcription into an abstract "thermodynamic geometry" at a time when the required vector and matrix techniques were not available. Let us therefore begin this description of the newer developments by reviewing the thermodynamic system of Gibbs.

Conjugate functions

The usefulness of a physical theory depends—to an extent that is perhaps insufficiently appreciated—on the mathematical form in which it finds expression. It is therefore interesting to touch on the close relationship in Gibbs's 1876 paper between the physical insights attained and the initial choice of mathematical formulation, particularly as Gibbs himself laid great stress on the proper choice of formal machinery.

Gibbs chose to consider the internal energy U as a function of the entropy S, volume V, and the mass quantities (often expressed as mole numbers) $N_1, N_2, \ldots, N_c$ of the c independent chemical components,

$$U = U(S, V, N_1, N_2, \ldots, N_c)$$

The temperature T and the pressure P of the equilibrium state are obtained as partial derivatives of U with respect to changes in entropy and volume:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots,N_c}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\ldots,N_c}$$

These equations associate an intensive variable R_i with each extensive argument X_i of the internal energy function $U = U(X_1, X_2, \ldots, X_{c+2})$:

$$R_i = \left(\frac{\partial U}{\partial X_i}\right)_{X_1\ldots X_{i-1}X_{i+1}\ldots X_{c+2}} \quad (1)$$

Because such relationships resemble the equations of classical mechanics that relate "conjugate" coordinates and momenta (with the internal energy U here taking the role of the Lagrangian function), it is now common to describe T as being (thermodynamically) *conjugate* to S, while $-P$ is similarly the conjugate of V.

Such conjugacy relationships naturally draw attention to the possible significance of the partial derivatives of U with respect to its remaining arguments N_i. Gibbs denoted these quantities, respectively conjugate to the mass quantities N_i, as the "chemical potentials"

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_1\ldots N_{i-1}N_{i+1}\ldots N_c}$$

By this simple stroke, Gibbs was able to incorporate changes in the quantities of the chemical components—including the effects of chemical reactions—and made possible a full-fledged chemical thermodynamics.

The observed proportionality of U and of each of its arguments to the total extent of the system moreover allows us to write the Gibbs–Duhem equation[2]

$$SdT + Vd(-P) + \sum_{i=1}^{c} N_i d\mu_i = 0$$

among variables $T, P, \mu_1, \ldots, \mu_c$. Such an equation is valid for any homogeneous system. When two or more homogeneous phases coexist in heterogeneous equilibrium (for example, an ice cube in water at 0 deg C and atmospheric pressure), each of their individual Gibbs–Duhem equations represents an additional constraining relationship among T, P and the μ_i's, thereby successively reducing the number of degrees of freedom available to these variables. As if in an afterthought, Gibbs pointed out the implication that a system of c components and ν distinct phases could be left with no more than $c - \nu + 2$ degrees of freedom. This is the celebrated "Gibbs phase rule," which has so dominated analyses of heterogeneous equilibrium to this day.

A very interesting and characteristic aspect of Gibbs's approach is its geometrical and graphical flavor. Since the derivative of a function bears a simple relationship to the slope of its graph, the internal-energy function may be graphically represented as a surface in a multidimensional Cartesian coordinate system with axes that are labelled by the values of the extensive variables U, S, V and the N_i's. Because of equations 1, the tangents to this surface then yield the values of T, P and the μ_i's.

The capacity of such an "equilibrium surface" to make clear at a glance the solution of certain thermodynamic problems that had seemed almost impossible to solve so provoked the admiration of James Clerk Maxwell that he sent Gibbs a plaster model of such a surface, shown in figure 1.

Of course, Gibbs had been led initially[3] to his fundamental equation

$$U = U(S, V, N_1, \ldots, N_c)$$

on the basis of its special graphical

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qualities, which allowed him to exercise his unusual geometric abilities in the solution of thermodynamic problems. Gibbs appears to have had a strong intuition for the underlying role of geometry in thermodynamic theory; his general approach in many ways anticipates the trend towards the "geometrization of science," which continues unabated to this day.

Thermodynamic geometry

While Gibbs's skillful development of the graphical properties of the equilibrium surfaces was of great importance—especially in the two papers preceding his great third paper—we may observe that these surfaces are in a sense contrary to the spirit of his general approach, which is one of shifting attention away from overall processes to the properties of individual equilibrium states. An equilibrium surface, representing as it does the set of *all* such states, would require for its construction a vastly greater volume of information that would be necessary to describe some one particular state. While Gibbs's surfaces would, if available, certainly suffice to answer any thermodynamic question, such surfaces may not represent the useful thermodynamic relationships characteristic of some *specific* equilibrium state in the most simple, economical and transparent way.

Moreover, it has long been realized (initially by Gibbs himself) that the geometry of the Gibbsian surfaces lacks an important element of that word in its original sense: $\gamma\epsilon\omega$ = earth (area), $\mu\epsilon\tau\rho\iota\alpha$ = measure, hence "area-measure." This element is what mathematicians refer to as the "metric" property. Simply put, distances, angles, areas and other familiar notions of mensuration do not have a clear-cut intrinsic significance on such surfaces.

Consider, for example, three points located close together on the Maxwell surface, representing three distinct equilibrium states of water, as shown in figure 2. These points in general define a triangle the edges, internal angles and total area of which can be obtained by the usual mensuration techniques. Suppose now that another admirer of Gibbs, having a dislike for Cartesian coordinates, has prepared a different model of the equilibrium surface, as faithful to the thermodynamic properties of water as the first, but with its axes inclined at angles other than 90°. On this second surface the same three equilibrium states would define a triangle with edges, internal angles and total area that are in general not equal to the corresponding values obtained previously. Since by thermodynamic reasoning alone we can give no reason for preferring one model over the other we must conclude that such metric properties as lengths, angles and areas should not be ascribed intrinsic thermodynamic significance. What remains is an instance of the more primitive pregeometry of connectivity, which is sometimes referred to as "affine geometry" to distinguish it from the full "metric geometry" that is already known to second-year high-school students.

Is there a metric?

The surfaces (more generally *hypersurfaces*, since they often occupy more than two dimensions) of Gibbsian thermodynamics therefore represented a pioneering intrusion of geometrical concepts into physical theory, but lacked the metric qualities that are characteristic of more recent developments of this kind. As examples, one thinks immediately of the Riemann geometry that underlies modern gravitation theory or the Hilbert space of modern quantum theory, both of which have a fully developed metric structure. In quantum theory, for example, the probability amplitudes representing the predicted values of physical observables are obtained as scalar products (requiring lengths and separation angles) of abstract vectors in Hilbert space, so that one could hardly think of doing without the metric character of that space.

If we ask the mathematician what specific properties are required for some set of "geometric" objects to exhibit a metric structure, the reply is remarkably simple[4]:

Suppose that we had somehow defined a "distance" d_{ij} between "points" i and j. Then in any "triangle" of

The viewpoint of J. Willard Gibbs

The year 1976, the bicentennial of the United States, also marks, for thermodynamicists the world over, the 100th anniversary of a scientific event of distinctly American character. In May 1876, the first portion of Josiah Willard Gibbs's monumental memoir, "On the Equilibrium of Heterogeneous Substances," completed its appearance in the *Transactions of the Connecticut Academy of Arts and Sciences*[a,b], the obscure journal of an impoverished state academy. The scientific and technological impact of this remarkable paper can even now be scarcely measured. The discipline of physical chemistry owes its origin to the appearance of Gibbs's paper; so do various traditions in physics, biology, metallurgy, geology, mechanical engineering and other disciplines that are concerned, directly or indirectly, with the thermal properties of matter.

It is curious that this, perhaps America's single most important scientific paper, was written while American science was still in its infancy. Gibbs had graduated from Yale University in 1863 as only the second PhD in science (the first in engineering) in the United States. He assumed the newly created—but unpaid!—professorship of mathematical physics at Yale before his first scientific paper was published. The New Haven townspeople who contributed toward the printing costs of the great manuscript could have had no more inkling than did the scientific leaders of Europe of the genius that was about to reveal itself in that scientific outpost on the American continent. Gibbs's life and work is described in several major biographical studies.[c]

Thermodynamics before Gibbs still carried much of its heritage as a child of the steam engine and the machine age. Through the first half of the 19th century, as Gibbs has remarked,[d] "truth and error were in a confusing state of mixture." Gibbs dates the beginnings of a true science of thermodynamics to the 1850 memoir of Rudolf Clausius, which with "nice discrimination" sifted order out of confusion and led for the first time to a correct enunciation of the second law of thermodynamics. Early forms of the second law, including that of Clausius, were set firmly in the Carnot tradition, but by 1865 Clausius had recognized that thermodynamic laws could be given a mathematically more useful form when expressed in terms of a new concept, the *entropy*. Unlike heat or work, the quantity of entropy is a state property: a definite attribute of an equilibrium system. It is also, however, more abstract, lacking obvious perceptual or intuitive significance. Later work by Ludwig Boltzmann (who regarded Gibbs as the greatest synthetic philosopher since Isaac Newton) was to clarify the physical nature of entropy as a measure of molecular randomness. But Clausius had been able, in a manner specifically eulogized by Gibbs, to anticipate the formal role of entropy before its precise physical nature could be known, and thereby to bring the evolution of thermodynamic ideas an important step forward.

Gibbs himself seized upon the entropy concept, and set Clausius's succinct couplet at the head of his own paper:

> *Die Energie der Welt ist constant.*
> *Die Entropie der Welt strebt einem Maximum zu.*
>
> [The energy of the world is constant.
> The entropy of the world tends toward a maximum.]

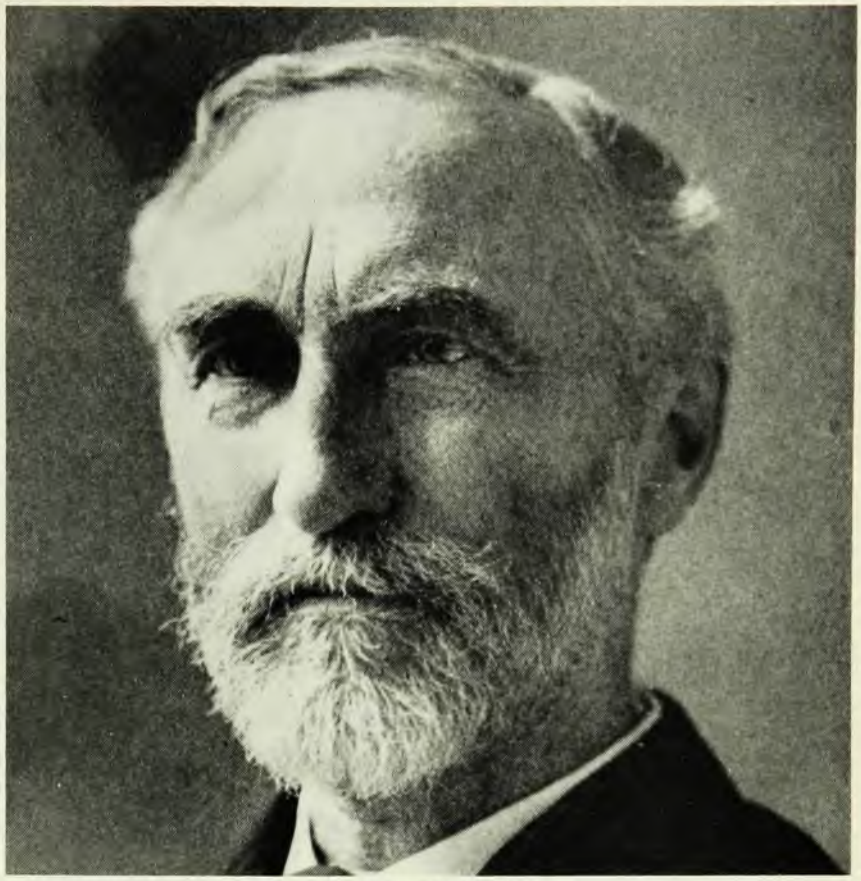
From these terse statements of the laws of thermodynamics, Gibbs embarks on a masterful investigation of their consequences along totally new lines. In the abstract to his work, he begins[e]:

> It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by no means escaped the attention of physicists, its importance does not appear to have been duly ap-

preciated. Little has been done to develop that principle as a foundation for the general theory of thermodynamic equilibrium.

The first sentence identifies the change of perspective—so simple, but of such fecundity—that is to open this new vista: Gibbs chooses to examine not the *processes* of thermodynamics (such as the cycles of the Carnot tradition), but rather the individual *states* of thermodynamic equilibrium. The maximization of entropy at constant energy (or, equivalently, the minimization of energy at constant entropy) is then sufficient to furnish the analytic characterization of the equilibrium state from which its thermodynamic description can be synthesized. There follows the rich succession of results: chemical potentials, phase rule, stability conditions, free energies, characterization of critical phases, equilibrium surfaces for heterogeneous substances and much more.

Although the approach chosen by Gibbs, with its complete departure from the language of Carnot cycles, was regarded as impenetrably complex by many of his contemporaries, there is evidence that Gibbs himself clearly perceived and valued its essential simplicity. Some years after the publication of his great paper but well before others were to begin developing the practical significance of his innovations, Gibbs expressed a viewpoint that was to recur in his studies on pure mathematics and statistical mechanics[f]: "One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity." He justified his approach to thermodynamics as one "... which seems more simple, and which lends itself more readily to the solution of problems, than the usual method ... Although my results were in a large measure such as had previously been demonstrated by other methods, yet, as I readily obtained those which were to me before unknown, I was confirmed in my belief in the suitableness of the method adopted."



J. WILLARD GIBBS

References

a. J. W. Gibbs, Trans. Conn. Acad. Arts Sci. **3,** 108 (1875–76).
b. *The Collected Works of J. Willard Gibbs,* Longmans, Green, New York (1928); reprinted by Dover, New York (1961), 2 volumes.
c. H. A. Bumstead, in reference *b*; M. Rukeyser, *Willard Gibbs,* Doubleday, Garden City, N.Y. (1947); L. P. Wheeler, *Josiah Willard Gibbs, The History of a Great Mind,* Yale U. P., New Haven (1962); R. J. Seeger, *Men of Physics: J. Willard Gibbs,* Pergamon, New York (1974).
d. J. W. Gibbs, Proc. Amer. Acad. **16,** 458 (1889); reference *b*, volume I, page 261.
e. J. W. Gibbs, Amer. J. Sci. **16,** 441 (1878); ref. *b*, volume I, page 354.
f. Letter of acceptance of the Rumford Medal (10 Jan. 1881); quoted in Wheeler, reference *c*, page 88.

points that might be selected, it need only be verified that no one side can exceed the sum of the other two sides; that is, the "triangle inequality"

$$d_{ij} \leq d_{ik} + d_{jk}$$

must be satisfied for all such sets of points.

The definition selected for d_{ij} might be very abstract and might appear to have nothing to do with "distance" in any ordinary sense. Yet, the mathematician assures us, if our choice has been fortunate enough to satisfy the triangle inequality, we are indeed entitled to treat d_{ij} as a distance in the ordinary Euclidean sense. The collection of "points" with this property is mathematically isomorphic to a Euclidean space.

It might seem unwise to raise such abstract notions in the context of thermodynamics, which is so deeply rooted in empirical principles. As Constantin Carathéodory once wrote,[5] it is remarkable to recognize that thermodynamics "... could be erected on foundations which were free of any hypothesis not subject to experimental verification." It is this empirical character that gives purely thermodynamic conclusions their great generality and rigor even in circumstances in which specific physical assumptions, such as those about the interactions of molecular constituents of the system, are liable to error. We recall the words of Gibbs from a related context[6]: "Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid."

The second law gives a length

Fortunately it is possible to move further along the path opened up by Gibbs and uncover, strictly within the confines of the empirical laws of thermodynamics, a full-fledged metric geometry of the abstract type described above. The detailed treatment of this geometry is of course carried out in mathematical terms,[1] but its main features can perhaps be more readily appreciated in a form that leaves off excessive technical detail.

To see how such a geometry might arise, let us consider some particular equilibrium state of a one-component system with its thermodynamic variables grouped into the usual conjugate pairs, (T, S) and $(-P, V)$. We may speak more generally of the ith pair, (R_i, X_i), as describing the ith mode of the system (thermal mode, mechanical mode, and so on).

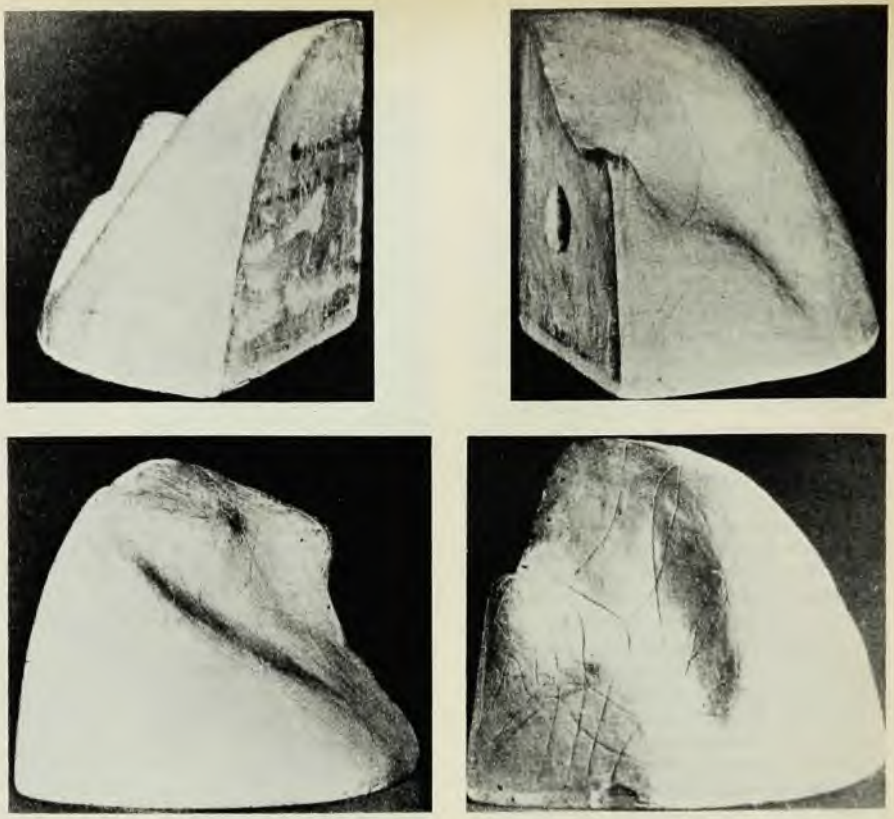
Now we know from everyday experience that as the entropy S of a system increases (for example, as heat is added), the temperature T can not decrease, and similarly, when a system is compressed in volume, the pressure it exerts can not diminish. (It is supposed in each case that the X_i variable not specifically mentioned is held constant during the change.) These observations are merely expressions of the second law of thermodynamics, any observation contrary to which could quickly be converted into some perpetual-motion device to solve the world's energy shortages! In general we should say that the *response* of the equilibrium system to any small increase in X_i is to increase (or at least never diminish) the associated conjugate R_i; more concisely, "the response of each R_i to its conjugate X_i is *positive*." Whereas the magnitude of the response will vary from state to state, its sign is fixed uniquely by the second law for every state. Because such intrinsic positivity is a characteristic of Euclidean distances, we may be encouraged somehow to think of the "response in R_i" as being related to the "length" of some abstract vector $\mathcal{R}_i$ describing the ith mode.

These speculations can only be pinned down by choosing some definition for the "length" $|\mathcal{R}_i|$ of such a vector and then checking whether this definition is compatible with the triangle inequality. The proper choice is to set $|\mathcal{R}_i|^2$ equal to the responsiveness of the ith mode, the partial derivative of R_i with respect to its conjugate X_i with the remaining X_j's held fixed,

$$|\mathcal{R}_i|^2 \equiv \left(\frac{\partial R_i}{\partial X_i}\right)_{X_1 \ldots X_{i-1} X_{i+1} \ldots X_{c+2}}$$

Similarly, to find the "separation" $d_{ij} = |\mathcal{R}_i - \mathcal{R}_j|$ of vectors $\mathcal{R}_i$ and $\mathcal{R}_j$, we must first find the variable that is conjugate to $R_i - R_j$ (the answer is not quite as simple as $X_i - X_j$, but is easily found), then measure how the quantity $R_i - R_j$ adjusts when its conjugate variable is altered slightly. By a series of such measurements we accumulate a set of purported "distances" d_{ij} which characterize the equilibrium system. Do these distances all conform to the metric demands of the triangle inequality? Remarkably, they do.

That this must be so requires for its proof precisely those properties of the function $U(S, V, N_1, \ldots, N_c)$ that were inferred by Gibbs from the empirical laws of thermodynamics, or those that are implicitly required to state the laws in terms of such a function. (See the Box on page 28.) The triangle inequality then serves as the condition that the measured responses should be consistent with the empirical laws of thermodynamics in all respects. Seen in this light, the laws of thermodynamics are nothing more nor less than the mathematical requirements for a metric geometry!



Model of the thermodynamic surface for water, presented to Gibbs by James Clerk Maxwell in 1875. It is now on permanent exhibit at the Gibbs Research Laboratory of Yale University. Maxwell's own copy of the model is at the Cavendish Laboratory of Cambridge University. Such equilibrium surfaces help clarify thermodynamic relationships. (Photo: Yale) Figure 1

Questions and answers

Let us see what this means in more concrete terms. Imagine that a geometer and a thermodynamicist occupy booths isolated from one another and from the outside except for slots through which written inquiries and replies can be passed. A questioner may request information from each booth through a typewriter console that simultaneously translates his questions into the separate languages of the geometer ("geometrical distances") and thermodynamicist ("thermodynamic responses"); these questions are to be acceptable only if they can be answered in some common language (such as pure numbers) by each respondent.

The questioner will find that he can in no way distinguish which booth holds which scientist, for the replies of the geometer are always in accordance with the principles of thermodynamics, just as those of the thermodynamicist are always in accordance with Euclid. If each were given a particular object for study—perhaps a molten alloy for the thermodynamicist, and an irregular tetrahedron for the geometer—the objects could be so chosen that requests for measured properties will always be answered by identical numerical replies from the two booths. In a sense, both scientists are studying the "same" object. Thermodynamics *is* geometry!

While this surprising formal isomorphism promises little help to the geometer, the same is by no means true for the thermodynamicist. The geometer would find little incentive to adopt the formalism of equilibrium thermodynamics to solve his mensuration problems, but the thermodynamicist may be startled by the ease with which thorny thermodynamic problems yield to the geometer's tools. To exploit this advantage, he will naturally use vector algebra in place of the partial differential equations, chain rules and cross-differentiation identities of the usual thermodynamic formalism. He may be initially disquieted that the "laws of thermodynamics" have somehow disappeared (they remain only implicitly in the mathematical structure being employed), but he will soon notice that his deductions are always fully consistent

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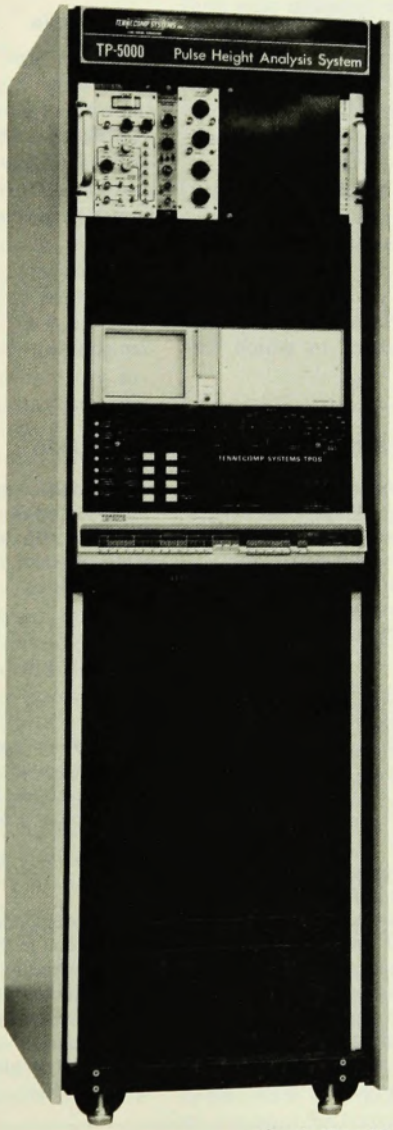

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with those laws so long as he "does geometry" according to the usual Euclidean rules.

Drawing the perpendiculars

Before illustrating these ideas, it may be helpful to remark on the general form in which certain familiar elements of Gibbs's formalism reappear in this abstract geometric picture. The thermodynamic vectors of the geometric representation belong to some abstract n-dimensional Euclidean space. This means that in order to locate each point of the space uniquely, it is necessary to employ a coordinate system having n independent axes. Any n independent vectors $\mathcal{R}_1, \mathcal{R}_2, \ldots, \mathcal{R}_n$ (representing n independent thermodynamic variables $R_1, R_2, \ldots, R_n$) might be chosen to construct such a coordinate system, each such vector pointing along one of the proposed axes.

Unlike the familiar Cartesian axes, however, the chosen vectors will not generally be mutually perpendicular unless some very special choice of thermodynamic variables has been made. But if $\mathcal{R}_1$ (say) is not perpendicular to $\mathcal{R}_2, \mathcal{R}_3, \ldots, \mathcal{R}_n$, we can always find the unique direction that *is* perpendicular to these other axes. We label a vector along this direction as $\bar{\mathcal{R}}_1$, and choose its length so that the scalar product of $\mathcal{R}_1$ and $\bar{\mathcal{R}}_1$ (the product of their lengths times the cosine of their separation angle) is unity. By similar reasoning we can find vectors $\bar{\mathcal{R}}_2, \bar{\mathcal{R}}_3, \ldots, \bar{\mathcal{R}}_n$, where each $\bar{\mathcal{R}}_i$ lies perpendicular to all the vectors $\mathcal{R}_j$ (except $\mathcal{R}_i$ itself), and the lengths are chosen such that the scalar product of $\mathcal{R}_i$ and $\bar{\mathcal{R}}_i$ is unity for each i. Figure 3 illustrates this process in three dimensions. It shows also that this new set of vectors bears a close geometrical relationship to the former set, in the sense that if we had begun with the vectors $\bar{\mathcal{R}}_i$, we should have been led uniquely by the above procedure to the original vectors $\mathcal{R}_i$, and *vice versa*.

The new vectors must of course be associated with some corresponding thermodynamic variables $\bar{R}_i$, and it is then natural to ask how these new variables are related to the initial R_i's. It turns out that $\bar{R}_i$ and R_i are *conjugates* in the sense in which that term was used previously. Thus the conjugacy relationship of the Gibbsian formalism reappears as a kind of perpendicularity requirement in the abstract geometry. As in ordinary plane geometry, drawing the perpendiculars often turns out to be a useful device for analyzing the figures that arise in a thermodynamic context. Just as Gibbs was motivated to study the chemical potential because it is conjugate to the mass of a chemical component, a variable of interest, so one will generally find it convenient to introduce the conjugates $\bar{R}_i$ of whatever variables R_i have been chosen (out of convenience or necessity) to represent the state of a system.

We might inquire how the dimensionality n of the abstract thermodynamic space is to be determined. A moment's reflection will suggest that this dimensionality must correspond to the number of "degrees of freedom" in the Gibbsian sense, and this indeed turns out to be the case. The dimensionality is therefore fixed by Gibbs's phase rule, $n = c - \nu + 2$, and so depends on the number of phases and of independent chemical components present in the system. The appearance of a *new* phase ($\upsilon \rightarrow \upsilon + 1$), for example, is associated with a collapse of the dimensionality ($n \rightarrow n - 1$) of the abstract thermodynamic space, a process with interesting ramifications, both geometrically and thermodynamically.

Although I have not described their form in Gibbs's formalism, I have mentioned certain "stability conditions" that the second law enforces on the measured values of thermodynamic properties. In the geometric formalism these conditions are merely the statement that the cosine of any (thermodynamic) angle must lie between plus and minus one. Of course, Euclidean geometry would never permit any statement to the contrary, so the general consistency of thermodynamic deductions with these stability constraints is rather easily attended to in the metric space.

It may also be helpful to remark briefly on the general *physical* significance of these abstract lengths and angles: The length of $\mathcal{R}_i$ is a measure of the responsiveness of the system to changes in the associated extensive parameter X_i: the extent to which the system adjusts its value of R_i in response to a small change in X_i. For example, the length of the temperature vector $\mathcal{T}$ depends, as well as on the temperature T, on the reciprocal of the constant-volume heat capacity of the system, and that of the pressure vector $\mathcal{P}$ depends on its inverse compressibility. The angle θ_{ij} between vectors $\mathcal{R}_i$ and $\mathcal{R}_j$, on the other hand, measures the extent to which different responses are *coupled*, that is, to what extent a small change in the extensive variable X_i of the ith mode will produce a response R_j in the jth mode and *vice versa*. The angle between the temperature and pressure vectors, for example, is related to a thermal-expansion coefficient.

The metric parameters, unlike those of a phase space, therefore have an *intrinsic* thermodynamic significance, since they are uniquely associated with measured physical properties of the particular system under discussion. The lengths of the thermodynamic vectors depend on the physical units in which the associated responses are measured, but the "coupling" angles θ_{ij} do not.

An example

Let us now illustrate some of these ideas more concretely with the simple example of a one-component fluid, say a sample of water. The system will be discussed in terms of such standard experimental properties as the constant-pressure and constant-volume heat capacities,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P, \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

the constant-temperature and constant-

The thermodynamics–geometry connection

The key empirical observations that a formal theory of equilibrium thermodynamics must undertake to incorporate, and draw inferences from, include:

▶ **The first law** Internal energy is a conserved state function, satisfying the mathematical requirement for an exact differential,

$$\frac{\partial R_i}{\partial X_j} = \frac{\partial R_j}{\partial X_i}$$

▶ **The second law** Internal energy is minimized in the isolated equilibrium state,

$$\frac{\partial R_i}{\partial X_i} \geq 0$$

Implicit in these statements is the empirical observation that permits such "laws" to be expressed in terms of U.

▶ **The properties of an equilibrium system** may be associated with low-order derivatives of a mathematical function U, which involves only a small determinate number of independent state properties and is sufficiently "smooth" to permit the application of the partial differential calculus in the usual manner.

On the other hand, a set of vectors $\mathcal{R}_i$ will obey the triangle inequality if their scalar product $\langle \mathcal{R}_i | \mathcal{R}_j \rangle$ always satisfies the postulates

▶ $\langle \mathcal{R}_i | \mathcal{R}_j \rangle = \langle \mathcal{R}_j | \mathcal{R}_i \rangle$

▶ $\langle \mathcal{R}_i | \mathcal{R}_i \rangle \geq 0$

▶ $\langle \mathcal{R}_i | \mathcal{R}_j + \mathcal{R}_k \rangle = \langle \mathcal{R}_i | \mathcal{R}_j \rangle + \langle \mathcal{R}_i | \mathcal{R}_k \rangle$

These three postulates can be brought into correspondence with the three empirical laws above by defining the thermodynamic scalar product as

$$\langle \mathcal{R}_i | \mathcal{R}_j \rangle \equiv \frac{\partial R_i}{\partial X_j}$$

The correspondence will then be readily appreciated in the first two cases and can be made evident for the third by detailed consideration of the distributive character of the "chain rules" of the partial differential calculus.

For a complete discussion see reference 1 below.

entropy compressibilities

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \quad \beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

and the thermal expansion coefficient,

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The abstract space of any one-component fluid has only two dimensions, so the thermodynamic geometry of this system can be represented in the plane diagram of figure 4. This figure depicts the temperature vector $\mathcal{T}$ and pressure vector $\mathcal{P}$ together with their conjugates, the entropy vector $\mathcal{S}$ and volume vector $\mathcal{V}$, respectively, with the lengths and separation angles expressed in terms of the standard properties defined above. Note that in this case the perpendicularity relationships that define the conjugate vectors simply mean that $\mathcal{S}$ is perpendicular to $\mathcal{P}$, and $\mathcal{V}$ to $\mathcal{T}$.

An inspection of figure 4 readily reveals that the angles $\theta_{\mathcal{ST}}$ and $\theta_{-\mathcal{PV}}$ must satisfy

$$\cos^2\theta_{\mathcal{ST}} = \cos^2\theta_{-\mathcal{PV}}$$

which translates to the thermodynamic identity

$$C_P/C_V = \beta_T/\beta_S$$

Similarly, the obvious relationship

$$\sin^2\theta_{\mathcal{ST}} + \cos^2\theta_{\mathcal{ST}} = 1$$

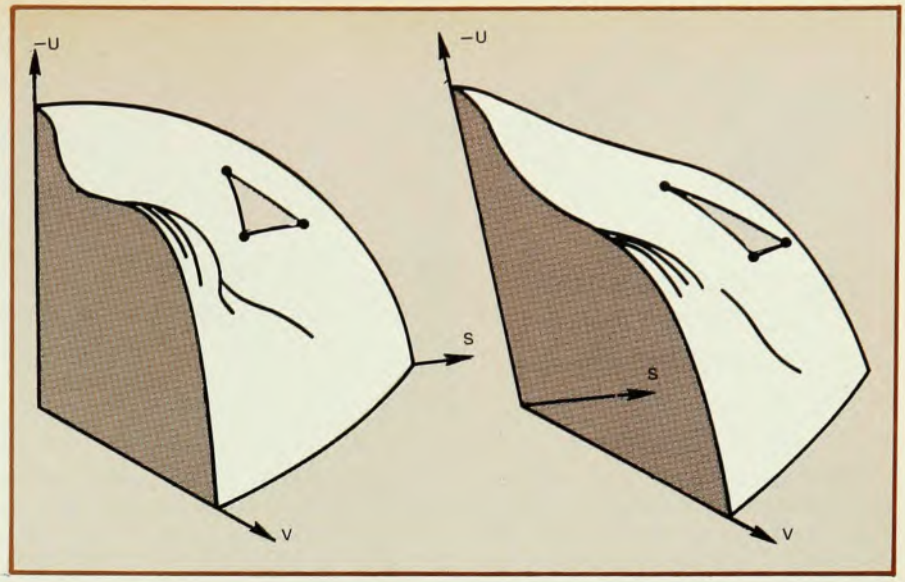
becomes the thermodynamic identity

$$C_P = C_V + TV\alpha_P^2/\beta_T$$

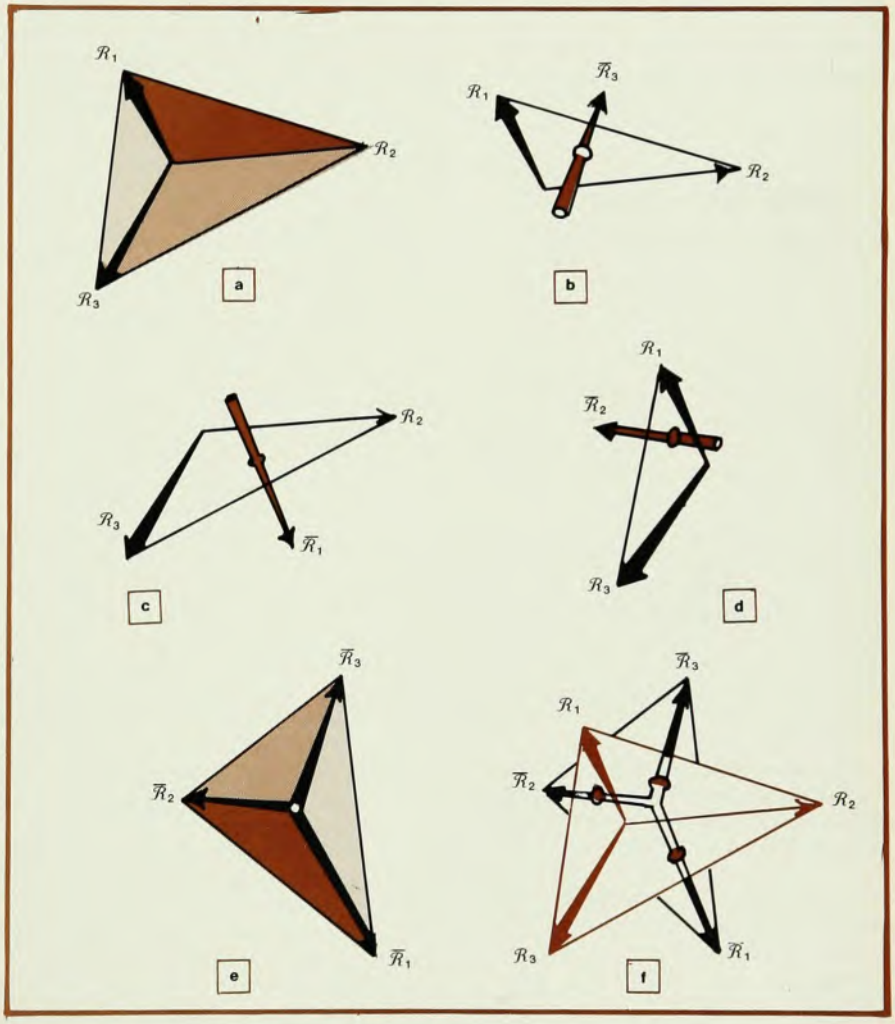
and other well known identities can immediately be read off from the geometry of the figure by the appropriate transformation relations. Moreover, the impossibility of cooling a sample of water held at constant volume so as to produce an equivalent temperature increase in a similar sample held at constant pressure (corresponding to the well known thermodynamic stability condition, $C_P \geq C_V$) can be recognized to follow from the geometric requirement, $\cos^2\theta_{\mathcal{ST}} \leq 1$, and so forth.

Other features

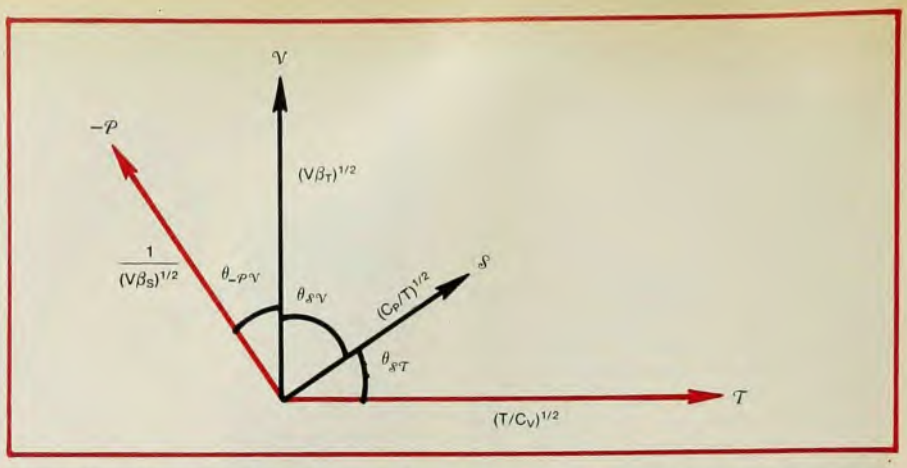
The geometric techniques enjoy a general advantage that is not suggested by the above simple example but becomes readily apparent in more complex systems. This advantage stems from the fact that the geometry of Euclidean spaces can be developed in a form that is essentially independent of their dimensionality n. Because thermodynamic dimensionality and chemical complexity are related by Gibbs's phase rule, the theorems and procedures that can be developed from the geometric formalism turn out to apply with little or no modification to systems of arbitrary chemical complexity—in contrast to the procedures used in the usual formalism, which are often quite difficult to apply to systems of more than a few components.



A triangle of equilibrium states on the thermodynamic surface of figure 1. When the Cartesian system of Maxwell's model (left) is replaced by a skewed coordinate system (right), lengths, angles and area change: The surface lacks the "metric" property. Figure 2



How conjugate thermodynamic vectors are constructed is illustrated for a three-dimensional system such as a binary alloy. The vectors $\mathcal{R}_1$, $\mathcal{R}_2$, $\mathcal{R}_3$ might represent responses to thermal, mechanical and chemical disturbances; they form an irregular tetrahedron (**a**). The vector $\overline{\mathcal{R}}_3$ conjugate to $\mathcal{R}_3$ must be perpendicular to the plane of the other two vectors, as shown in **b**; its length must be such that the scalar product of the conjugate vectors is unity. The three new vectors form a conjugate tetrahedron, **e**, shown interpenetrating the original tetrahedron in **f**; this suggests the complementary character of the construction. Figure 3



Thermodynamic vectors for a simple fluid are represented in a two-dimensional diagram in which lengths and angles are expressed in terms of such experimental properties as heat capacities; for example, $\cos\theta_{\mathcal{S}\mathcal{V}} = \alpha_P[TV/C_P\beta_T]^{1/2}$ and $\cos\theta_{\mathcal{S}\mathcal{T}} = [C_V/C_P]^{1/2}$. The thermodynamically conjugate temperature and volume vectors, $\mathcal{T}$ and $\mathcal{V}$, are perpendicular; so are the pressure vector $\mathcal{P}$ and the entropy vector $\mathcal{S}$. A number of thermodynamic relationships among the experimental quantities can be read off directly from the diagram. Figure 4

A shortcoming of the abstract Euclidean geometry outlined so far is that it describes only the isolated equilibrium state and thereby neglects more global aspects of a thermodynamic description. These would be useful in treating general changes of state: processes, cycles and so on. To obtain this more global perspective, we must regard the abstract vectors of the local description as functions of the state of the system. These thermodynamic vectors then stretch, shrink or rotate as we move from point to point on a Gibbsian surface, making the abstract Euclidean geometry itself a function of state.

This circumstance might appear to complicate hopelessly a general geometric description, and to remove any semblance of fundamental significance that might have been claimed on its behalf. A mathematician would, however, recognize in this situation a classic example of a *Riemann geometry*, that form of metric geometry that describes "curved" spaces. At every point of a Riemann space the geometry is locally "flat" (Euclidean); this property has previously been exploited in the description of individual equilibrium states. Perhaps the study of more global aspects of the abstract Riemann geometry can provide additional insights into thermodynamic behavior, particularly in the neighborhood of critical points (states of incipient breakup into distinct phases, where heat capacities and other properties may appear to become infinite) and other anomalies on the Gibbs surface.

The abstract geometric theory may be regarded as giving an interesting alternative representation of the underlying thermodynamic regularities which Gibbs, in an analytic framework, had already comprehended in an essentially complete fashion. The geometric and analytic characterizations of an equilibrium state are complementary, in somewhat the same manner as Heisenberg matrix mechanics and Schrödinger wave mechanics form complementary representations, in quite dissimilar mathematical languages, of a single underlying quantum theory.[7]

In thermodynamics, just as in quantum mechanics, the interplay between the dissimilar mathematical representations further illuminates the underlying structure of the theory. We can likewise expect the new representation to add to the arsenal of practical techniques that can be brought to bear on the analysis of the thermal properties of matter. In this way we move one step closer to "... the point of view from which the subject appears in its greatest simplicity."

* * *

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References

1. F. Weinhold, J. Chem. Phys. **63,** 2479, 2484, 2488, 2496 (1975); **65** (1976) (to be published).
2. H. B. Callen, *Thermodynamics,* John Wiley, New York (1960), page 48.
3. J. W. Gibbs, Trans. Conn. Acad. Arts Sci. **2,** 309, 382 (1873); *The Collected Works of J. Willard Gibbs,* Longmans, Green, New York (1928); Dover, New York (1961); volume I, pages 1, 33.
4. P. Dennery, A. Krzywicki, *Mathematics for Physicists,* Harper and Row, New York (1967), page 109.
5. C. Carathéodory, Math. Ann. **67,** 355 (1909).
6. J. W. Gibbs, *Elementary Principles of Statistical Mechanics,* Dover, New York (1960), preface.
7. J. von Neumann, *Mathematical Foundations of Quantum Mechanics,* Princeton U. P., Princeton, N.J. (1955). □