

XVI. STATISTICAL THERMODYNAMICS*

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RESEARCH OBJECTIVES

The purpose of this project is to carry thermodynamics beyond its classical limitations. There are several factors that make the extension of the traditional framework possible, the most important of which may be summarized as follows.

The well-known universal principles of thermodynamics do not form a complete basis for a rigorous establishment of the theory; it is necessary to formulate additional assumptions concerning the properties of material systems, such as the existence of homogeneous phases, validity of equations of state, and the like.

Within judiciously chosen limitations, a set of basic assumptions can be expressed in terms precise enough to generate a mathematical theory with desirable properties. Some of the limitations of the theory can be overcome by the formulation of sets of successively more refined postulates. These generate theories that are adequate for dealing with the more exacting requirements. Thus thermodynamics becomes a master scheme, consisting of a number of closely knit deductive systems devised for different types of situations.

Two systems of this sort have been developed in detail, thus far, and the study of another is in a preliminary state. The first is the thermostatic theory of phase equilibrium, which follows essentially Gibbsian lines with certain innovations. The definition of homogeneous phases has been changed to include symmetry properties. This led to a significant generalization of the classical phase rule. Also, a new kind of geometrical interpretation of the thermostatic formalism was established, an example of which is discussed in this report.

The second theory deals with the statistical aspects of equilibrium. It was investigated primarily by P. M. Quay.

A detailed account of the first theory is ready for publication. A second paper on the statistical theory is being prepared.

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A. THE GEOMETRICAL INTERPRETATION OF THE THERMOSTATIC STABILITY CONDITIONS

It has been pointed out (1) that the thermostatic formalism can be given a mathematical interpretation in terms of affine geometry. The most interesting aspect of the geometrical interpretation of a physical theory is that the geometry is characterized by a group of transformations, the invariants of which are likely to be of physical interest. We consider an example to show that the geometrization of thermostatics gives rise to a physically meaningful theory of invariants.

Let

$$u = u(x_1, x_2, \dots, x_r) \tag{1}$$

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be the fundamental equation of a homogeneous phase referred to a system of fixed size. For the sake of definiteness, we may keep the volume fixed, and interpret Eq. 1 as the energy density, expressed as a function of the densities of the extensive variables. Equation 1 represents a surface in the space x_1, x_2, \dots, x_r, u that is called the Gibbs space. The stability of the system is determined essentially by the quadratic form

$$w = \sum_1^r u_{ik} \xi_i \xi_k \quad (2)$$

which appears in the expansion of the fundamental equation. Here

$$u_{ik} = \frac{\partial^2 u}{\partial x_i \partial x_k} = \frac{\partial P_i}{\partial x_k} \quad (3)$$

$$\xi_i = \delta x_i$$

and P_i is the intensity conjugate to x_i .

In points of normal stability the quadratic form in Eq. 2 is positive definite. As Gibbs (2) has already stated, this leads to the conditions

$$\lambda_k = \left(\frac{\partial P_k}{\partial x_k} \right) P_1 P_2 \dots P_{k-1} x_{k+1} \dots x_r > 0 \quad k = 1, 2, \dots, r \quad (4)$$

We do not consider here points of critical stability, in which the form of Eq. 2 is singular.

The substitution of specific thermodynamic variables in Eq. 4 makes it apparent that each λ_k has an intuitive physical meaning. A complete proof of Eq. 4 requires an elementary, but somewhat abstruse, algebra. This can be elucidated by a geometrical interpretation provided by affine geometry.

We propose to transform w to the diagonal form

$$w = \sum_1^r \lambda_k \eta_k^2 \quad (5)$$

There are infinitely many nonsingular linear (affine) transformations,

$$\xi = T\eta \quad (6)$$

that diagonalize a quadratic form. Equation 5, involving the coefficients λ_k , is obtained by imposing the condition that the determinant of the transformation T be +1. Such transformations are called unimodular, or equiaffine. In affine geometry they are the counterparts of the orthogonal transformations of Euclidian geometry. Equiaffine transformations leave volume elements invariant, but lengths and angles have no invariant meaning. The coefficients λ_i are somewhat similar to eigenvalues, but there are

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also marked differences.

A unimodular transformation satisfying the requirements stated above can be constructed stepwise by the well-known method of "completing the square":

$$\begin{aligned}
 w &= \sum_1^r u_{ik} \xi_i \xi_k = u_{11} \left(\xi_1 + \frac{1}{u_{11}} \sum_2^r u_{1k} \xi_k \right)^2 \\
 &\quad - \frac{1}{u_{11}} \left(\sum_2^r u_{1k} \xi_k \right)^2 + \sum_2^r u_{ik} \xi_i \xi_k \\
 &= \lambda_1 \eta_1^2 + w_1(\xi_2, \xi_3, \dots, \xi_r)
 \end{aligned} \tag{7}$$

where $\lambda_1 = u_{11}$,

$$\eta_1 = \xi_1 + \frac{1}{u_{11}} \sum_2^r u_{1k} \xi_k \tag{8}$$

and w_1 is a quadratic form of only $(r-1)$ variables. This procedure can be continued, and leads to Eq. 5. The transformations of the type of Eq. 8 consist of subtracting the multiple of the i^{th} row and column from the j^{th} row and column, where $j > i$. Hereby the principal minors $D_k = \det |u_{ij}|$ with $i, j = 1, 2, \dots, k$ are unaltered. Thus

$$D_k = \lambda_1 \lambda_2 \dots \lambda_k \tag{9}$$

and

$$\lambda_k = \frac{D_k}{D_{k-1}} \tag{10}$$

By writing the minors as Jacobians, we have

$$D_k = \frac{\partial(P_1 P_2 \dots P_k)}{\partial(x_1 x_2 \dots x_k)} \tag{11}$$

Equation 10 is easily reduced to the form of Eq. 4.

For the case of two variables, $r = 2$, the foregoing transformation is represented in Fig. XVI-1. This figure is the affine mapping of Fig. XVI-2. We recall that affine transformations preserve parallelism, but not orthogonality. The orthogonal diameters $A'A'_1$, $B'B'_1$ are mapped into so-called conjugate diameters AA_1 , BB_1 . For equiaffine transformations, the square $O'A'B'C'$ is mapped into the parallelogram $OABC$ of equal area.

Figure XVI-1 is to be constructed in the following sequence: Obtain A as the

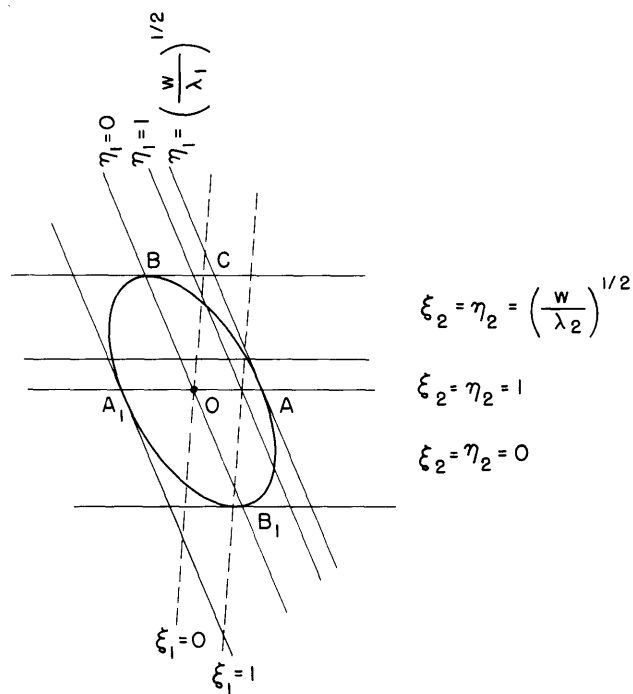


Fig. XVI-1. Equiaffine transformation $\xi_1, \xi_2 \rightarrow \eta_1, \eta_2$ that diagonalizes the quadratic form represented by the ellipse.

intersection of the conic (ellipse) with the axis ξ_1 , construct tangent AC and the parallel diameter BB_1 . The tangent in B is parallel to OA.

The generalization to many dimensions is straightforward, provided that the rules of working with oblique coordinates are observed. Such coordinate systems are specified by the families of parallel hyperplanes: $\xi_i = \text{constant}$ ($i=1, 2, \dots, r$). With orthogonal coordinates, each family of parallel planes is uniquely represented by their normal. This short cut is not available for oblique coordinates. The axis ξ_1 is now defined as the intersection of the plane $\xi_2 = 0, \xi_3 = 0, \dots, \xi_r = 0$.

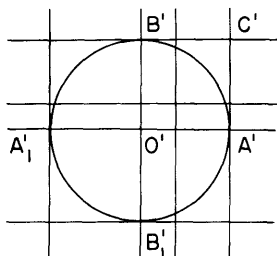


Fig. XVI-2. Equiaffine mapping of Fig. XVI-1 to orthogonal axes.

Although the line OA represents both the ξ_1 and the η_1 axes, the planes $\xi_1 = \text{constant}$ and $\eta_1 = \text{constant}$ are different from each other. If x_1 is interpreted as the entropy, the planes $\xi_1 = \text{constant}$ and $\eta_1 = \text{constant}$ correspond to processes at constant entropy and temperature, respectively. The peculiarity of the thermodynamic formalism, that the variables to be kept constant have to be

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especially indicated, appears to be the consequence of the use of oblique coordinate systems. This situation is unaffected by the ingrained habit of drawing the diagrams in Gibbs space with orthogonal axes.

It is evident from either Fig. XVI-1 or Eq. 4 that the λ_1 are not invariant. Thus different coefficients are obtained if the variables are relabeled, for example, $\xi_1 = \delta n$, $\xi_2 = \delta S$, instead of $\xi_1 = \delta S$, $\xi_2 = \delta n$, where n is the number of moles per unit volume.

However, the determinant

$$D_r = \lambda_1 \lambda_2 \dots \lambda_r \quad (12)$$

is an equiaffine invariant, a quantitative measure of the stability of the system. Geometrically $(D_r)^{-1/2}$ is the area OABC for the ellipse $w = 1$.

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References

1. L. Tisza, The differential geometrical formalism of thermostatics, Quarterly Progress Report No. 54, Research Laboratory of Electronics, M. I. T., July 15, 1959, p. 149.
2. J. W. Gibbs, Collected Works, Vol. I (Yale University Press, New Haven, 1948), p. 110.

ERRATA for "The Thermodynamic Theory of Line Singularities in One-Component Systems," Quarterly Progress Report No. 55, October 15, 1959, pages 135-138:

Page 135, Eq. 1 should read:

$$G(p, T) = g(p) + (T-T_\lambda) f(p) + h(T-T_\lambda) \quad (1)$$

where $g(p)$ is a slowly varying function of pressure. The rest of the symbols were defined correctly. The second derivatives g'' and f'' are neglected.

The other formulas follow through straightforward differentiation. Thus the analogs of Ehrenfest's relations (page 136) should read:

$$V \alpha \zeta = \frac{C_p}{T} + f' \zeta \quad (10)$$

$$V \kappa_T \zeta = V \alpha + f' \quad (11)$$

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