

XII. STATISTICAL THERMODYNAMICS*

Prof. L. Tisza

A. THE DIFFERENTIAL GEOMETRICAL FORMALISM OF THERMOSTATICS

It is well known that the problems of phase stability can be geometrically interpreted in terms of the curvature of the fundamental surface in the thermodynamic phase space spanned by the extensive variables (Gibbs space). It has been pointed out (1) that the thermostatic formalism can be given a mathematical interpretation in terms of affine differential geometry.

Further investigation has shown that some of the basic concepts of this geometry correspond to significant thermostatic concepts. A review of this correspondence between geometrical and thermostatic concepts is not practicable in the present report, chiefly because the concepts of affine geometry cannot be assumed to be generally known.

The purpose of this report is, primarily, to indicate the relation of the affine theory of curvature to the better-known approaches to the same problem.

The elementary theory of curvature considers a two-dimensional surface in three-dimensional Euclidean space. Interest is directed toward properties that are invariant under congruence transformations.

According to a second point of view, the surface is characterized by a Riemannian metric and is discussed without reference to an embedding space.

The affine theory differs in a subtle way from both classical theories. All these theories are easily generalized to the case of n-dimensional surfaces.

We consider an n-dimensional surface represented in terms of n parameters u^1, u^2, \dots, u^n as follows:

$$\vec{x} = \vec{x}(u^1, u^2, \dots, u^n) \quad (1)$$

where

$$\vec{x} = [x^1, x^2, \dots, x^{n+1}] \quad (2)$$

is a vector in an (n+1)-dimensional Euclidean space. We introduce a vector pointing along the normal of the surface:

*This research was supported in part by the U.S. Air Force (Office of Scientific Research, Air Research and Development Command) under Contract AF49(638)-95. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(XII. STATISTICAL THERMODYNAMICS)

$$\vec{\xi} = \begin{vmatrix} \vec{e}_1 & \vec{e}_2 \cdots \vec{e}_{n+1} \\ x_1^1 & x_1^2 \cdots x_1^n \\ \vdots & \vdots \\ x_n^1 & x_n^2 \cdots x_n^n \end{vmatrix} \quad (3)$$

where the \vec{e}_i are mutually orthogonal unit vectors and

$$x_k^a \equiv \frac{\partial x^a}{\partial u^k} \quad (4)$$

The elementary theory of curvature is based on the two fundamental forms:

$$ds^2 = \sum_{i,k} g_{ik} du^i du^k \quad \text{I}$$

$$-d\vec{x} \cdot d\vec{\xi} = \sum_{i,k} h_{ik} du^i du^k \quad \text{II}$$

Here ds^2 is the square of the line element,

$$g_{ik} = \sum_a x_i^a x_k^a \quad (5)$$

and

$$h_{ik} = \left(\vec{x}_{ik}, \vec{x}_1, \vec{x}_2, \dots, \vec{x}_n \right) \quad (6)$$

where

$$\vec{x}_k = \frac{\partial \vec{x}}{\partial u^k}, \quad \vec{x}_{ik} = \frac{\partial^2 \vec{x}}{\partial u^i \partial u^k} \quad (7)$$

The right-hand side of Eq. 6 is the $(n+1)$ by $(n+1)$ determinant, consisting of the elements of the vectors in parentheses.

Fundamental form I represents the intrinsic metric of the surface, and fundamental form II expresses the curvature with respect to the embedding space. Both forms are needed to determine the principal radii of curvature R_1 and R_2 . However, according to a fundamental theorem of Gauss, the product $R_1 R_2$ depends solely on form I, and it is invariant with respect to bending – an operation that preserves the metric but changes form II. This theorem is the basis for the presentation of Riemannian geometry in terms of the metric tensor g_{ik} only.

In affine geometry we investigate the properties of the surface that are invariant under the linear transformations

$$x^i = \sum_{k=1}^{n+1} a_k^i x^k \quad (8)$$

We further require that the determinant of Eq. 8 be unity, in order to preserve the volume spanned by the $n + 1$ vectors. Transformations of this sort do not preserve length, and metric form I becomes meaningless.

However, it is easily shown from Eq. 6 that form II is invariant under volume-preserving linear transformations. Moreover, it was shown by G. Pick and W. Blaschke (2) that a satisfactory differential geometry can be built on the basis of the tensor h_{ik} .

Although there are far-reaching similarities between the role of the tensors g_{ik} and h_{ik} , there are also essential differences. The transformations (Eq. 8) do not preserve the length of a vector and the angle between two vectors. Therefore such important concepts as "orthogonality" and "normal to a surface" lose their meaning. The interesting point is that these concepts can be replaced by others, such as "conjugate direction," and "affine normal," which allow development of the theory to a degree that is quite comparable with the classical theories.

The significant aspect of these results, from the present point of view, is that the peculiarities of affine geometry have their counterpart in thermostatics, and, in fact, also in irreversible thermodynamics (3).

In Gibbs space the coordinates x^i are interpreted as the extensive variables: energy, entropy, volume, and the mole numbers of the chemical components. A vector $\Delta\vec{x}$ in this space corresponds to a process in which these quantities change in definite proportions. This is indeed the characteristic feature of such processes as phase transitions and chemical reactions. Processes underlying the change of a single extensive variable

$$\begin{aligned} \Delta x^i &\neq 0 & i &= k \\ \Delta x^i &= 0 & i &\neq k \\ & & i &= 1, 2, \dots, n+1 \end{aligned} \quad (9)$$

are most artificial, and it is more practical to work in terms of the basic processes that are characteristic of each system. This is what is achieved by the affine transformations given in Eq. 8.

The problem is being further studied.

L. Tisza

References

1. L. Tisza, Geometrization of thermostatics, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., April 15, 1958, p. 100.
2. Cf. W. Blaschke, Vorlesungen über Differentialgeometrie, Vol. I (Berlin, 3rd ed., 1930); Vol. II (Berlin, 1923).
3. The formal analogy between thermostatics and irreversible thermodynamics that is the basis for this interpretation is discussed in Quarterly Progress Report No. 52, Jan. 15, 1959, p. 130.