

## V. STATISTICAL THERMODYNAMICS\*

Prof. L. Tisza  
A. D. Pierce

### RESEARCH OBJECTIVES

In common usage the terms "statistical thermodynamics" and "statistical mechanics" are either considered synonyms, or are meant to reflect a difference in emphasis only. In the present project these terms are used to denote complementary logical structures with partially overlapping ranges of application. The exact nature of this complementary relation is itself an object of study and has been repeatedly restated.

The common problem confronting the statistical theories is to overcome the limitations of macroscopic thermodynamics. While this theory accounts for the gross aspects of chemical structure, it provides only the sketchiest dynamic description of the structure of matter in space time.

Both statistical theories aim to increase the detail of space-time description, but their procedures for introducing it into the theory are radically different.

In classical statistical mechanics one chooses a hypothetical starting point corresponding to the most complete space-time description: matter is assumed to consist of interacting, invariant point masses the motion of which is described in terms of precisely defined trajectories. The excessive detail of this description is eliminated partly by statistical averaging and partly by a series of quantum conditions.

In the statistical thermodynamics proposed here the elements of space-time specification are added only stepwise to the macroscopic theory. Each step in this approximation is organized as a tightly knit deductive system that closely corresponds to a segment of the over-all experimental situation.

Thermodynamic systems are defined as conjunctions of spatially disjoint volume elements (subsystems), each of which is characterized by a set of additive conserved quantities (invariants) – the internal energy and the mole numbers of the independent chemical components. The coupling between any two subsystems is brought about by the exchange of additive invariants. Such transfers are called thermodynamic processes. The coupling between two subsystems may be switched on and off by the removal or insertion of an appropriate type of wall that is restrictive or nonrestrictive for a specific type of transfer.

In general, the additive invariants of a composite system can be classified into fixed and free variables, according to whether or not they are fixed by the existing constraints.

The macroscopic thermodynamics of equilibrium (briefly, MTE)<sup>1</sup> is the deductive system that forms the first stage of our approximation procedure. Under equilibrium conditions, the free variables fluctuate around constant values. In MTE only these constant values are considered, and are obtained from the maximization of the entropy for given values of the fixed variables.

In the statistical thermodynamics of equilibrium (briefly, STE)<sup>2</sup> it is assumed that the free variables are independent random variables and their probability distribution function is determined by the fixed variables.

The manipulations of the constraints (walls, catalysts, inhibitors) trigger processes leading to new equilibria. By iterating the sequence of operation and process, it is possible to build up complex and well-determined processes out of the simple irreversible steps.

Thus the theory contains a rudimentary time concept. The system is described within the frame of a discontinuous space-time manifold, in which the time intervals are terminated when constraints are relaxed. These must be far enough apart so that the previous process has come to a standstill.

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For a more detailed temporal description it is necessary to consider the correlations of the random variables. This is to be undertaken by quantum-mechanical methods.

A quantum-mechanical problem that may be relevant for describing a type of strong correlations is reported on here.

The comparison of statistical thermodynamics and statistical mechanics calls for the reconsideration of such questions as the ergodic hypothesis, the problem of dissipation and the connection between entropy and information. A detailed report on these conceptual problems is in preparation.

L. Tisza

### References

1. L. Tisza, *Ann. Phys.* 13, 1 (1961).
2. P. M. Quay and L. Tisza, Statistical thermodynamics of equilibrium (a paper being prepared for publication).

### A. ELECTRON-VIBRATION INTERACTION AND THE GENERALIZED BORN-OPPENHEIMER APPROXIMATION

Problems in molecular and solid-state physics often start with a Schrödinger equation in terms of nuclear coordinates in which electrons enter only indirectly inasmuch as the electronic energy acts as the potential energy for the nuclear motion. We call the Hamiltonian underlying this Schrödinger equation a quasi-Hamiltonian, to distinguish it from the exact particle Hamiltonian containing the interactions of all electrons and nuclei.

The transition from the particle Hamiltonian to the quasi-Hamiltonian is conveyed by the adiabatic, or Born-Oppenheimer approximation. In its original form, however, this approximation has its limitations. Its application is justified only if the relevant electronic state is nondegenerate and if the spacing between electronic levels is not small. These conditions are not fulfilled in metals. Nevertheless, the standard method works well enough for most problems in the theory of metals, and the effects caused by electron-lattice interaction may be explained by familiar perturbation methods.

Only the phenomenon of superconductivity gives indication of a breakdown of the Born-Oppenheimer method. Indeed, the Bardeen, Cooper, Schrieffer, and equivalent theories can be considered as implicit corrections to the Born-Oppenheimer approximation in which the unusually strong coupling of the lattice and electrons is taken into account. The inapplicability of the standard method to superconductivity does not mean that there is a major breakdown in the Born-Oppenheimer approximation, but it does indicate that a modification of this approximation is needed.

Such modifications were indeed devised some time ago by Renner<sup>1</sup> in the case of linear molecules, and by Moffitt and Liehr,<sup>2</sup> Longuet-Higgins et al.<sup>3</sup> for nonlinear molecules (dynamic Jahn-Teller effect).

We have developed a general formalism from which the previously considered

problems follow as special cases.

Although the motivation of this work was mainly an extension of the theory to solids, only a semiphenomenological study of an exploratory character has been carried out thus far. Further details can be found in the thesis of Arthur D. Pierce.<sup>4</sup>

L. Tisza

References

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4. A. D. Pierce, *Electron-Lattice Interaction and the Generalized Born-Oppenheimer Approximation*, Ph.D. Thesis, Department of Physics, M.I.T., January 1962.

