

XIII. STATISTICAL THERMODYNAMICS*

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A. THEORY OF PHASE EQUILIBRIUM

It was pointed out in the Quarterly Progress Report of April 15, 1957, page 167, that the scope of Gibbs' phase theory can be significantly extended by including the specification of symmetry in the definition of a homogeneous phase. However, the new definition cannot be used efficiently in conjunction with the traditional formulation of thermodynamic postulates (1). Instead, a more appropriate set of definitions and postulates has been found, which can be outlined as follows.

Isolated thermodynamic systems tend toward states of equilibrium that consist of a small number of homogeneous regions in space called "phases." The systems are described in terms of the independent variables Q^1, Q^2, \dots , which are interpreted as the energy, the volume, and the mole numbers of the independent components.

The precise definition of homogeneous phases in equilibrium is implicit in the following postulates:

I. The independent variables Q^i are additive:

$$Q^i = \sum_a Q_a^i \quad (1)$$

where the index a refers to spatially separated subsystems, such as different phases or volume elements. The Q^i are also called "extensive parameters."

II. A homogeneous phase in equilibrium is formally represented by a primitive fundamental equation

$$S_a = S^{\zeta_a} \left(Q_a^1, Q_a^2, \dots \right) \quad (2)$$

which is a first-order homogeneous function with continuous derivatives of at least the second order. The superscript ζ_a denotes the symmetry character of the phase a .

III. The entropy S of the system is

$$S(Q^1, Q^2, \dots) = \max \left\{ \sum_a S^{\zeta_a} \left(Q_a^1, Q_a^2, \dots \right) \right\} \quad (3)$$

The maximum is taken under the constraints provided by Eq. 1 with the Q^i as constants.

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DEFINITION:

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad (4)$$

where T is the temperature.

IV. The temperature varies over the range $0 < T < \infty$.

V. For all phases in equilibrium near absolute zero,

$$\lim_{T \rightarrow 0} S^{\zeta^a} = 0$$

While the traditional formulation deals with quasi-static processes in order to arrive eventually at state functions, the present version considers equilibrium states exclusively. We have a postulational foundation of thermostatics, and the discussion of processes is relegated to irreversible thermodynamics. This splitting of classical thermodynamics into more sharply delimited special theories can be carried even farther. Thus, the five postulates imply that thermodynamic stability is independent of the size of the system. This result is, indeed, a salient feature of phase equilibrium, although it fails for very small systems (droplets) and also for very large ones (stars). For such cases the present postulates have to be modified.

Within the clearly understood limits of validity, the postulates form the basis of a rigorous phase theory. It is not necessary to introduce ad hoc assumptions which render the existing thermodynamic theories unreliable.

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References

1. For a recent formulation, with bibliography, cf. P. T. Landsberg, *Revs. Modern Phys.* 28, 363 (1956).

B. CANONICAL DISTRIBUTION FOR INDEPENDENT RANDOM VARIABLES

The purpose of the present report is to develop a statistical theory of fluctuations which, in the limit of vanishing fluctuations, reduces to the phenomenological theory of Section XIII-A. However, the theory is not confined to the Gaussian approximation, which is valid for small fluctuations only. With the terminology introduced in the Quarterly Progress Report of April 15, 1957, page 166, we shall derive an I_c theory centered around the canonical distribution of independent random variables.

The standard procedure for the derivation of the canonical distribution involves the introduction of statistical concepts into classical or quantum mechanics. Szilard (1) followed an entirely different course. He developed a unified statistical thermodynamics

by formulating a statistical generalization of the classical thermodynamic postulates. His fundamental results remained largely unnoticed in thermodynamics literature. Recently, the question was reopened and further developed by Mandelbrot (2), who pointed out that Szilard's argument can be considered as an instance of estimation theory of mathematical statistics.

The ideas of Szilard and Mandelbrot tie in particularly well with the new axiomatization of thermostatics discussed in Section XIII-A. The objective of our program is to develop a self-contained theory along these lines. The discussion is divided into a number of successive stages, the first of which can be outlined as follows.

Let us consider a thermodynamic system specified by the extensive parameters Q^i introduced in Section XIII-A. All but one of these parameters are to be held fixed, while the coupling with the surroundings produces fluctuations of the energy, which is now a random variable U that takes on values denoted by u . The case of several random variables will be discussed later.

As idealized surroundings we consider reservoirs $R(t)$, where t denotes an arbitrary temperature scale defined by the following stipulation: if, on establishing a coupling between $R(t_1)$ and $R(t_2)$, on the average, energy flows from the $R(t_1)$ to $R(t_2)$, then $t_1 > t_2$.

We formulate the following postulates:

I. The values u of the random variable U are distributed according to some probability density function $P(u/t)$ that depends parametrically on the temperature t and the fixed parameters of the system.

II. Two closed systems with the same fixed parameters and the same energy u are thermodynamically equivalent regardless of the temperatures of the reservoirs with which they had been in contact.

III. Composition rule. The energy of a composite system is the sum of the energies of its parts and the partial energies are statistically independent. Briefly, the energies are additive random variables.

From these assumptions we can derive that

$$P(u/t) = g(u)e^{-\beta(t)u}/Z(\beta) \quad (1)$$

where $g(u)$ is a "structure function" that depends only on the properties of the system, $\beta = \beta(t)$ is a function of temperature only. The definition $T = 1/k\beta$ can be shown to lead to the thermodynamic temperature T , and k is Boltzmann's constant. The partition sum $Z(\beta)$ is determined from the normalization of the probability.

The structure function $g(u)$ can be identified with the degree of degeneracy of the energy as obtained from the solution of the Schrödinger equation of the system. It is noteworthy that the existence of the structure function can be inferred from the general statistical postulates I, II, and III without any explicit reference to atomic structure.

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In addition to the canonical distribution we can also consider the microcanonical distribution of systems with fixed values of all the extensive parameters, including the energy. The foregoing definition of the temperature concept can be extended to microcanonical distribution by means of a "maximum likelihood estimate" (2).

The conditions of the equivalence of the canonical and microcanonical methods are now being studied.

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References

1. L. Szilard, *Z. Physik* 32, 753 (1925).
2. B. Mandelbrot, Transactions of the 1956 Symposium on Information Theory, M.I.T., Cambridge, Massachusetts, Sept. 10-12, 1956; cf. E. T. Jaynes, *Phys. Rev.* 106, 620 (1957).