XIX. STATISTICAL THERMODYNAMICS[*]

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A. OUTLINE OF PROJECT

In this project the term "statistical thermodynamics" will be used in a sense that is distinct from "statistical mechanics." The random variables of statistical mechanics are the specifications of the system in mechanical phase space. In statistical thermodynamics the random variables are points in thermodynamic phase space spanned by the extensive parameters: internal energy U, entropy S, volume V, and the mole numbers N_j of the independent components.

There are various physical models that are described in terms of these thermodynamic random variables; for example, a system in contact with reservoir supplying energy, mass, and so forth. Or, we may consider the open subsystem of a closed thermodynamic system in equilibrium.

Statistical thermodynamics is meant to be a loose generic term which includes a number of theories that can be classified partly according to the type of probability distribution considered, and partly according to the detail in which the statistical information is utilized.

We shall assume that either the values of the thermodynamic quantities observed at successive instances of time are independent random variables or that they form Markov chains. (The probability distribution at one instant determines the probability at later instants.) We shall refer to these two theories by the symbols I and M.

From another point of view, we shall distinguish between theories which establish relations involving the first, the second, or the higher moments of the distribution. This is summarized in the following table.

	First Moment	Second Moment	Higher Moments
I	I1	I2	Ic
M	M1	M2	

Establishing relations among the first moments of the probability distribution leads to phenomenological theories: I1 is thermostatics, M1 irreversible thermodynamics. The higher moments can be obtained from the canonical distributions; hence the notation Ic.

We note that the canonical distributions form the connecting link between the present method, and that of statistical mechanics. The reduction of the theory to molecular quantities is within the purview of statistical mechanics.

The second moments of the distribution are already correctly given by means of the gaussian approximation to the canonical distribution. Hence the special role of the second column in our table.

In Section XIX-B we report on work that aims at the systematic development of I1. Another work on Ic has been started. The Gaussian theory, I2, is a special case which is of no great interest if a canonical theory is available.

Two papers which can be classified as M2 theories were completed before the project started (1, 2).

The major goal of the project is to establish an Mc theory, i.e., a canonical distribution within the realm of irreversible processes. It is believed that such a development would open up the possibility of new applications.

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References

1. L. Tisza and I. Manning, Phys. Rev. (March 15, 1957). This paper contains a bibliography of M2 theories.
2. A. E. Fein, Ph.D. Thesis, to be presented to the Department of Physics, M.I.T.

B. GENERALIZED PHASE RULE AND SUPERFLUIDITY

According to recent precision measurements (1) the specific heat of liquid helium exhibits a logarithmic singularity at the λ-point. This result does not fit into the well-known Ehrenfest classification of phase transitions of higher order (2). Moreover, viscosity measurements (3) seem to indicate a singularity that is inconsistent with the assumption of a second-order transition.

Originally, Ehrenfest proposed the idea of higher-order transitions to describe an experimental situation in conflict with the phase rule.

The purpose of this report is to attack the problem from a more fundamental point of view. We shall show that Gibbs' theory of thermodynamic stability can be sharpened and that it leads to a modified phase rule which includes the observed λ-point singularities (4).

The main point of the argument is the redefinition of the concept of phase so that it will include a statement of its symmetry properties.

A homogeneous phase can be formally defined by means of the fundamental equation

$$U = U_\zeta (Q_1, Q_2, \cdots Q_{c+2}) \tag{1}$$

where U is the internal energy, and the Q_k represents the other extensive parameters: the entropy S, the volume V, and the mole numbers of the c independent components. The new feature is the subscript ζ which specifies the symmetry of the phase. For a crystal, ζ identifies the space group. For an isotropic fluid, it refers to the full linear group of translations and rotations.

One of the parameters in Eq. 1, say Q_{c+2}, is taken to determine the size of the system. The c + 1 variables, $q_k = Q_k/Q_{c+2}$, specify the intrinsic properties. We say that the system has variance $\delta_1 = c + 1$.

Generally speaking, Eq. 1 does not always satisfy the requirements of stability, and the system may break up into a number of homogeneous phases. The intensive parameters (pressure P, temperature T, and chemical potentials μ) are constant throughout the heterogeneous system.

If we compare two coexisting phases, the following situations may occur:

q_k $\diagdown$ ζ	identical	distinct
identical	single phase	liquid-vapor
distinct	twin phases	polymorphic phases

Of the three two-phase situations, the case of identical q_k and distinct ζ is the new feature added to the classical theory. It arises if two phases are energetically identical and transform into each other by means of an operation such as reflection or inversion. Adapting well-known terminology from crystallography, we speak of twin phases. Domains of opposite polarization in ferromagnetism and ferroelectricity can also be considered as twin phases.

The occurrence of twin phases becomes important in connection with critical phenomena. A critical point is defined as "a state in which two phases (the conjugate phases) become identical."

It can be shown (4) that critical points have a singular character and that such thermodynamic coefficients as C_p, α, and κ_T (specific heat, expansion coefficient, and compressibility) become infinite.

It can be shown, moreover, that the number of degrees of freedom of the critical points is

$$\delta_2 = c - 1 + \sigma \tag{2}$$

where σ is a symmetry number that is equal to 1, if the conjugate phases are twin

phases, and zero otherwise.

For the ordinary liquid-vapor critical point, $c = 1$, $\sigma = 0$, and $\delta_2 = 0$; that is, we have an isolated critical point.

The λ-points of one-component systems are obtained for $c = 1$, $\sigma = 1$, $\delta_2 = 1$. We have a λ-line; that is, a transition temperature T_0 is obtained for an entire range of pressures.

It is easily seen that the ideas outlined provide a satisfactory scheme for the λ-transitions in crystals.

The case of liquid helium calls for some special remarks. Thermodynamically, the helium λ-point is in no way different from the λ-transitions in solids. The foregoing theory applies if we assume $\sigma = 1$ for helium. This means that the superfluid state of helium should exist in two twin modifications which are energetically equivalent (i.e., with the same q_k) and which transform into each other by means of a symmetry operation such as reflection or inversion.

This conclusion is surprising and not compatible with any of the microscopic models suggested, thus far, for helium. The problem could be accepted as solved only if a wave function with the lower symmetry were actually constructed. Obviously, this calls for much more powerful methods than those used in the present phenomenological argument.

A detailed presentation of this work is being prepared for publication.

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References

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2. P. Ehrenfest, Leiden Comm. Suppl. 75b (1933).

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4. Some of the ideas presented here were already advanced in L. Tisza, On the general theory of phase transitions, Technical Report 127, Research Laboratory of Electronics, M.I.T., June 15, 1949; contribution to J. E. Mayer, R. Smoluchowski, and W. A. Weyl, Phase Transformations of Solids (John Wiley and Sons, Inc., New York, 1951), p. 1.