XV. STATISTICAL THERMODYNAMICS[*]

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RESEARCH OBJECTIVES

In recent years various authors have noted that statistical thermodynamics can be derived from general statistical assumptions without the specification of a statistical mechanical model. Our research project is devoted to the systematic development of this idea. A thermodynamic system is a region of space specified by its volume, energy, and mass content (including its chemical composition). If an isolated thermodynamic system is subdivided into parts that are allowed to exchange energy and/or mass, these quantities become random variables. They exhibit rapid fluctuations around values which drift slowly toward asymptotic equilibrium levels. The study of the asymptotic values is the objective of classical thermostatics. The systematic approach has yielded new results even in this case, as described in Section XV-A. The fluctuation around equilibrium may be described by assuming that the values of the fluctuating quantities at discrete intervals of time are independent random variables. This assumption leads to a theory that is similar to that of the canonical and microcanonical ensembles in statistical mechanics, but contains less mechanical and more statistical detail.

Finally, the drift toward equilibrium and the time-dependent aspects of fluctuations are discussed by means of a theory in which the random variables form Markov chains. Thus far, we have considered Markov processes almost exclusively in the Gaussian approximation. Only a simple combinatorial model was in the non-Gaussian category. This line of thought is to be pursued in the near future.

A. SECOND PHASE RULE AND SUPERFLUIDITY

A theory of phase equilibrium has been recently reported (1, 2). Its essential feature is a new definition of the phase concept which requires specification of its symmetry. This theory leads to a relation (3) which might be called the "second phase rule." It plays a role for λ-anomalies that is similar to the role of the first phase rule for first-order transitions.

The application of the second phase rule to the helium λ-line yields the following theorem.

THEOREM: If the λ-line of helium represents a locus of singularities of the specific heat C_p in the p-T plane, the second phase rule requires that the superfluid state exist in two modifications that are related to each other by a binary symmetry operation.

The experiments of Buckingham, Fairbank, and Kellers (4) provide convincing evidence for a singularity of the specific heat at the saturated vapor pressure. There are reasons to believe that the λ-point has a similar character even under higher pressure, although a direct experimental check would be desirable.

If we assume tentatively the existence of a line of singularities, our theorem requires that the ground-state wave function of helium be doubly degenerate.

This conclusion contradicts the existing quantum-mechanical theories for helium, which assume that the ground-state wave function is nondegenerate. While this conclusion might be invalidated by a negative result of the aforementioned experiment, it is still pertinent to ask, How reliable is our theorem? This question has many sides, since there is no general agreement on the basic assumptions of phase theory and the admissible rules of inference. A partial list of the problems that we have investigated follows.

The most important basic assumptions of the theory were listed previously (2). These include, in addition to the laws of thermodynamics, the assumptions that the system consists of homogeneous parts and that the energy of spatially disjoint sub-systems is additive. These assumptions are of limited validity, but they are quite justified in the case of helium. However, in the case of superconductivity, the magnetic interaction of current elements is in contradiction to strict additivity, and hence the application of the theory calls for special considerations. The same is true of other transitions involving magnetization or electric polarization.

In the existing thermodynamic theories of phase transitions there are two procedures that are objectionable and render the conclusions unreliable. The first is the method of power-series expansion. This method is indispensable in the study of stability with respect to small displacements, but becomes questionable at the critical point. The expansion of the Gibbs function around a critical point is demonstrably wrong. This is not so obvious in the expansion of the internal energy.

We have made a detailed study of this matter, but shall not report it, since we found that expansion techniques are always unsatisfactory in the critical region. It is therefore important to note that the derivation of the second phase rule does not require such expansions and depends only on the topological properties of thermo-dynamic phase space.

The second objectionable procedure is the well-known Maxwell rule of equal areas, which is generally used in connection with the van der Waals equation. This procedure is often believed to be an integral part of thermodynamic phase theory; at the same time, it is justly criticized for involving integration over a region of essential instability (5). Actually, this method can be avoided by using Gibbs' construction: the instable parts of the fundamental surface in the thermodynamic U-S-V space are replaced by a ruled surface representing the two-phase region.

It is interesting to point out the rationale for the use of the Maxwell rule. The application of Gibbs' construction requires a knowledge of the fundamental equation, which is equivalent to the equation of state, and also of the specific-heat function $C_p = C_p(T)$ at a fixed pressure. If these functions are known, the coexisting states of the liquid

and vapor may be connected by integration around the critical point within the stable range of the fluid. In the conventional treatment of the van der Waals condensation the $C_p(T)$ function is unspecified; instead, information is supplied concerning the essentially instable range of the system. This information is spurious; it has no theoretical basis and could not be supported by any conceivable experiment.

Our conclusion is that the second phase rule rests on solid ground and may be applied to helium, provided that direct experiments confirm the existence of a line of singularities.

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References

1. L. Tisza, Generalized phase rule and superfluidity, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., April 15, 1957, p. 167.

2. L. Tisza, Theory of phase equilibrium, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., July 15, 1957, p. 117.

3. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., April 15, 1957, p. 168; see Eq. 2.

4. M. J. Buckingham, W. M. Fairbank, and C. F. Kellers, International Conference on Low Temperature Physics and Chemistry, University of Wisconsin, Madison, Wisconsin, August 1957.

5. L. Van Hove, Revs. Modern Phys. 29, 200 (1957).