

XVII. STATISTICAL THERMODYNAMICS*

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RESEARCH OBJECTIVES

The purpose of this project is to develop thermodynamics in a systematic fashion from its foundations and to go beyond the scope of the classical theory by obtaining results of a structural and statistical character. The structural elements that serve as building blocks for the construction of complex thermodynamic systems are homogeneous phases specified primarily by such extensive variables as the energy, entropy, volume, and mole numbers of the independent components. This specification is satisfactory in the classical theory, which is concerned only with the energetic coupling of the system with macroscopic devices (engines and heat reservoirs). In the present theory, the point emphasized is whether or not two phases are distinguishable. This criterion makes it necessary to introduce symmetry operations together with intrinsic coordinates that serve to distinguish, say, right and left quartz, which are not distinguished in terms of the extensive variables. The introduction of symmetry has led to a significant extension of the classical theory of phase equilibrium.

Although the ultimate reduction of homogeneous phases to the constituent particles is left to statistical mechanics, in statistical thermodynamics the local values of the extensive variables are considered as random variables. This procedure leads to a large number of problems which are being studied in systematic fashion.

A. THE RELATION OF IRREVERSIBLE THERMODYNAMICS AND THERMOSTATICS

It is well known that the macroscopic theory of thermoelectric effects has to proceed along the lines of irreversible thermodynamics (1). The most conspicuous result of this theory is the correct derivation of the relations originally obtained by Kelvin from quasi-thermodynamic reasoning. The relation of the two methods has been repeatedly discussed (1, 2). The usual procedure is to translate the quasi-thermodynamic proof into the language of irreversible thermodynamics. The next step is to show that the correct result is obtained by reasoning that is equivalent to Onsager's reciprocity relations, which cannot be rigorously justified within thermostatics.

We propose to consider the relation of the two methods from a somewhat different angle. The thermostatic method will appear as an approximation to the correct procedure, and a quantitative expression is obtained for gauging the error involved in the approximation.

We follow the standard procedure and consider two thermodynamic systems in constrained equilibrium connected by a resistor. For small deviations from equilibrium, the entropy is

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$$\Delta S = -\frac{1}{2} \sum S_{ik} a_i a_k \quad (1)$$

Confining ourselves to two variables, we interpret the variables $a_1 = \delta U$ and $a_2 = \delta n$ as the deviations of the energy and of the mole numbers (say, of the electrons) from unconstrained equilibrium.

We define the "forces" as

$$\gamma_i = \sum S_{ik} a_k \quad (2)$$

where

$$S_{ik} = \frac{\partial^2 S}{\partial a_i \partial a_k} \quad (3)$$

It follows from the two laws of thermodynamics that

$$S_{ik} = S_{ki} \quad (4)$$

We have, in particular, $\gamma_1 = \delta(1/T)$ and $\gamma_2 = -\delta(\mu/T)$, where T and μ are the temperature and chemical potential, respectively.

According to the phenomenological equations of irreversible thermodynamics

$$\gamma_i = \sum_k R_{ik} \dot{a}_k \quad (5)$$

where the \dot{a}_k are the fluxes, and the elements of the resistance matrix R_{ik} can be expressed in terms of the electric and heat resistivity and the thermopower. According to the Onsager reciprocity relation

$$R_{ik} = R_{ki} \quad (6)$$

We introduce the transfer entropy S^* , defined by

$$TS^* = -\frac{R_{12}}{R_{11}} - \mu \quad (7)$$

This expression directly gives the Peltier heat. Moreover, it follows from Eq. 7 that S^* is the thermopower.

According to the proposed formulation of the thermostatic approximation, the analysis is based on Eq. 2 rather than on Eq. 5. The Kelvin relations follow (incorrectly) from Eq. 4 rather than from Eq. 6. Moreover, we obtain the thermostatic approximation \tilde{S} for the thermopower, defined by

$$T\tilde{S} = -\frac{S_{12}}{S_{11}} - \mu \quad (8)$$

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In order to estimate the quantitative importance of the use of irreversible thermodynamics, we have to consider concrete models. From the free-electron theory we obtain, for example,

$$\frac{S^*}{\tilde{S}} = \frac{2}{3} \left(1 + \frac{1}{2} \frac{d \ln \ell}{d \ln v} \right) \quad (9)$$

where ℓ is the mean free path and v is the average velocity. According to the standard assumption $\ell \sim v^4$, and hence

$$S^* = 2\tilde{S} \quad (10)$$

Much higher values can be obtained if "phonon drag" effects are important.

On the other hand, the thermomechanical effect of helium in very thin capillaries is rigorously given by thermostatics. The use of irreversible thermodynamics (1) only obscures the important fact that the process is, in this case, reversible.

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References

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2. H. B. G. Casimir, *Revs. Modern Phys.* 17, 343 (1945).