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Elementary Principles in Statistical Mechanics

Developed with Especial Reference to the Rational Foundation of Thermodynamics

Josiah Willard Gibbs

Cambridge University Press

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ELEMENTARY PRINCIPLES

IN

STATISTICAL MECHANICS

DEVELOPED WITH ESPECIAL REFERENCE TO

THE RATIONAL FOUNDATION OF THERMODYNAMICS

BY

J. WILLARD GIBBS
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PREFACE.

THE usual point of view in the study of mechanics is that where the attention is mainly directed to the changes which take place in the course of time in a given system. The principal problem is the determination of the condition of the system with respect to configuration and velocities at any required time, when its condition in these respects has been given for some one time, and the fundamental equations are those which express the changes continually taking place in the system. Inquiries of this kind are often simplified by taking into consideration conditions of the system other than those through which it actually passes or is supposed to pass, but our attention is not usually carried beyond conditions differing infinitesimally from those which are regarded as actual.

For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity.

Such inquiries have been called by Maxwell *statistical*. They belong to a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles, and of which Clausius, Maxwell, and Boltzmann are to be regarded as the principal founders. The first inquiries in this field were indeed somewhat narrower in their scope than that which has been mentioned, being applied to the particles of a system, rather than to independent systems. Statistical inquiries were next directed to the phases (or conditions with respect to configuration and velocity) which succeed one another in a given system in the course of time. The explicit consideration of a great number of systems and their distribution in phase, and of the permanence or alteration of this distribution in the course of time is perhaps first found in Boltzmann's paper on the "Zusammenhang zwischen den Sätzen über das Verhalten mehratomiger Gasmoleküle mit Jacobi's Princip des letzten Multiplicators" (1871).

But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. Moreover, the separate study of this branch of mechanics seems to afford the best foundation for the study of rational thermodynamics and molecular mechanics.

The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results. The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact. This does not make them more difficult to establish than the approximate laws for systems of a great many degrees of freedom, or for limited classes of such systems. The reverse is rather the case, for our attention is not diverted from what is essential by the peculiarities of the system considered, and we are not obliged to satisfy ourselves that the effect of the quantities and circumstances neglected will be negligible in the result. The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, but they make a somewhat blind guide in our search for those laws. This is perhaps the principal cause of the slow progress of rational thermodynamics, as contrasted with the rapid deduction of the consequences of its laws as empirically established. To this must be added that the rational foundation of thermodynamics lay in a branch of mechanics of which the fundamental notions and principles, and the characteristic operations, were alike unfamiliar to students of mechanics.

We may therefore confidently believe that nothing will more conduce to the clear apprehension of the relation of thermodynamics to rational mechanics, and to the interpretation of observed phenomena with reference to their evidence respecting the molecular constitution of bodies, than the study of the fundamental notions and principles of that department of mechanics to which thermodynamics is especially related.

Moreover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. Yet any theory is obviously inadequate which does not take account of all these phenomena. Even if we confine our attention to the phenomena distinctively thermodynamic, we do not escape difficulties in as simple a matter as the number of degrees of freedom of a diatomic gas. It is well known that while theory would assign to the gas six degrees of freedom per molecule, in our experiments on specific heat we cannot account for more than five. Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.

Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid.

The matter of the present volume consists in large measure of results which have been obtained by the investigators mentioned above, although the point of view and the arrangement may be different. These results, given to the public one by one in the order of their discovery, have necessarily, in their original presentation, not been arranged in the most logical manner.

In the first chapter we consider the general problem which has been mentioned, and find what may be called the fundamental equation of statistical mechanics. A particular case of this equation will give the condition of statistical equilibrium, *i. e.*, the condition which the distribution of the systems in phase must satisfy in order that the distribution shall be permanent. In the general case, the fundamental equation admits an integration, which gives a principle which may be variously expressed, according to the point of view from which it is regarded, as the conservation of density-in-phase, or of extension-in-phase, or of probability of phase.

In the second chapter, we apply this principle of conservation of probability of phase to the theory of errors in the calculated phases of a system, when the determination of the arbitrary constants of the integral equations are subject to error. In this application, we do not go beyond the usual approximations. In other words, we combine the principle of conservation of probability of phase, which is exact, with those approximate relations, which it is customary to assume in the "theory of errors."

In the third chapter we apply the principle of conservation of extension-in-phase to the integration of the differential equations of motion. This gives Jacobi's "last multiplier," as has been shown by Boltzmann.

In the fourth and following chapters we return to the consideration of statistical equilibrium, and confine our attention to conservative systems. We consider especially ensembles of systems in which the index (or logarithm) of probability of phase is a linear function of the energy. This distribution, on account of its unique importance in the theory of statistical equilibrium, I have ventured to call *canonical*, and the divisor of the energy, the *modulus* of distribution. The moduli of ensembles have properties analogous to temperature, in that equality of the moduli is a condition of equilibrium with respect to exchange of energy, when such exchange is made possible.

We find a differential equation relating to average values in the ensemble which is identical in form with the fundamental differential equation of thermodynamics, the average index of probability of phase, with change of sign, corresponding to entropy, and the modulus to temperature.

For the average square of the anomalies of the energy, we find an expression which vanishes in comparison with the square of the average energy, when the number of degrees of freedom is indefinitely increased. An ensemble of systems in which the number of degrees of freedom is of the same order of magnitude as the number of molecules in the bodies with which we experiment, if distributed canonically, would therefore appear to human observation as an ensemble of systems in which all have the same energy.

We meet with other quantities, in the development of the subject, which, when the number of degrees of freedom is very great, coincide sensibly with the modulus, and with the average index of probability, taken negatively, in a canonical ensemble, and which, therefore, may also be regarded as corresponding to temperature and entropy. The correspondence is however imperfect, when the number of degrees of freedom is not very great, and there is nothing to recommend these quantities except that in definition they may be regarded as more simple than those which have been mentioned. In Chapter XIV, this subject of thermodynamic analogies is discussed somewhat at length.

Finally, in Chapter XV, we consider the modification of the preceding results which is necessary when we consider systems composed of a number of entirely similar particles, or, it may be, of a number of particles of several kinds, all of each kind being entirely similar to each other, and when one of the variations to be considered is that of the numbers of the particles of the various kinds which are contained in a system. This supposition would naturally have been introduced earlier, if our object had been simply the expression of the laws of nature. It seemed desirable, however, to separate sharply the purely thermodynamic laws from those special modifications which belong rather to the theory of the properties of matter.

J. W. G.

New Haven, December, 1901.

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