

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

CAMBRIDGE LIBRARY COLLECTION

Books of enduring scholarly value

Mathematical Sciences

From its pre-historic roots in simple counting to the algorithms powering modern desktop computers, from the genius of Archimedes to the genius of Einstein, advances in mathematical understanding and numerical techniques have been directly responsible for creating the modern world as we know it. This series will provide a library of the most influential publications and writers on mathematics in its broadest sense. As such, it will show not only the deep roots from which modern science and technology have grown, but also the astonishing breadth of application of mathematical techniques in the humanities and social sciences, and in everyday life.

Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs (1839–1903) was the greatest American mathematician and physicist of the nineteenth century. He played a key role in the development of vector analysis (his book on this topic is also reissued in this series), but his deepest work was in the development of thermodynamics and statistical physics. This book, *Elementary Principles in Statistical Mechanics*, first published in 1902, gives his mature vision of these subjects. Mathematicians, physicists and engineers familiar with such things as Gibbs entropy, Gibbs inequality and the Gibbs distribution will find them here discussed in Gibbs' own words.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

Cambridge University Press has long been a pioneer in the reissuing of out-of-print titles from its own backlist, producing digital reprints of books that are still sought after by scholars and students but could not be reprinted economically using traditional technology. The Cambridge Library Collection extends this activity to a wider range of books which are still of importance to researchers and professionals, either for the source material they contain, or as landmarks in the history of their academic discipline.

Drawing from the world-renowned collections in the Cambridge University Library, and guided by the advice of experts in each subject area, Cambridge University Press is using state-of-the-art scanning machines in its own Printing House to capture the content of each book selected for inclusion. The files are processed to give a consistently clear, crisp image, and the books finished to the high quality standard for which the Press is recognised around the world. The latest print-on-demand technology ensures that the books will remain available indefinitely, and that orders for single or multiple copies can quickly be supplied.

The Cambridge Library Collection will bring back to life books of enduring scholarly value (including out-of-copyright works originally issued by other publishers) across a wide range of disciplines in the humanities and social sciences and in science and technology.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

Elementary Principles in Statistical Mechanics

*Developed with Especial Reference to the
Rational Foundation of Thermodynamics*

JOSIAH WILLARD GIBBS



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore,
São Paulo, Delhi, Dubai, Tokyo

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org

Information on this title: www.cambridge.org/9781108017022

© in this compilation Cambridge University Press 2010

This edition first published 1902

This digitally printed version 2010

ISBN 978-1-108-01702-2 Paperback

This book reproduces the text of the original edition. The content and language reflect the beliefs, practices and terminology of their time, and have not been updated.

Cambridge University Press wishes to make clear that the book, unless originally published by Cambridge, is not being republished by, in association or collaboration with, or with the endorsement or approval of, the original publisher or its successors in title.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

Bale Bicentennial Publications

ELEMENTARY PRINCIPLES IN
STATISTICAL MECHANICS

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

Hale Bicentennial Publications

With the approval of the President and Fellows of Yale University, a series of volumes has been prepared by a number of the Professors and Instructors, to be issued in connection with the Bicentennial Anniversary, as a partial indication of the character of the studies in which the University teachers are engaged.

This series of volumes is respectfully dedicated to

The Graduates of the University

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

ELEMENTARY PRINCIPLES
IN
STATISTICAL MECHANICS

DEVELOPED WITH ESPECIAL REFERENCE TO

THE RATIONAL FOUNDATION OF
THERMODYNAMICS

BY

J. WILLARD GIBBS

Professor of Mathematical Physics in Yale University

NEW YORK: CHARLES SCRIBNER'S SONS

LONDON: EDWARD ARNOLD

1902

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

Copyright, 1902,

BY CHARLES SCRIBNER'S SONS

Published, March, 1902.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

P R E F A C E.

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.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

viii

PREFACE.

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 Multiplifiers" (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,

PREFACE.

ix

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.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

PREFACE.

xi

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

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

xii

PREFACE.

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.

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

CONTENTS.

CHAPTER I.

GENERAL NOTIONS. THE PRINCIPLE OF CONSERVATION
OF EXTENSION-IN-PHASE.

	PAGE
Hamilton's equations of motion	3-5
Ensemble of systems distributed in phase	5
Extension-in-phase, density-in-phase	6
Fundamental equation of statistical mechanics	6-8
Condition of statistical equilibrium	8
Principle of conservation of density-in-phase	9
Principle of conservation of extension-in-phase	10
Analogy in hydrodynamics	11
Extension-in-phase is an invariant	11-13
Dimensions of extension-in-phase	13
Various analytical expressions of the principle	13-15
Coefficient and index of probability of phase	16
Principle of conservation of probability of phase	17, 18
Dimensions of coefficient of probability of phase	19

CHAPTER II.

APPLICATION OF THE PRINCIPLE OF CONSERVATION OF
EXTENSION-IN-PHASE TO THE THEORY OF ERRORS.

Approximate expression for the index of probability of phase	20, 21
Application of the principle of conservation of probability of phase to the constants of this expression	21-25

CHAPTER III.

APPLICATION OF THE PRINCIPLE OF CONSERVATION OF
EXTENSION-IN-PHASE TO THE INTEGRATION OF THE
DIFFERENTIAL EQUATIONS OF MOTION.

Case in which the forces are function of the coördinates alone	26-29
Case in which the forces are functions of the coördinates with the time	30, 31

CHAPTER IV.

ON THE DISTRIBUTION-IN-PHASE CALLED CANONICAL, IN WHICH THE INDEX OF PROBABILITY IS A LINEAR FUNCTION OF THE ENERGY.

	PAGE
Condition of statistical equilibrium	32
Other conditions which the coefficient of probability must satisfy	33
Canonical distribution — Modulus of distribution	34
ψ must be finite	35
The modulus of the canonical distribution has properties analogous to temperature	35–37
Other distributions have similar properties	37
Distribution in which the index of probability is a linear function of the energy and of the moments of momentum about three axes	38, 39
Case in which the forces are linear functions of the displacements, and the index is a linear function of the separate energies relating to the normal types of motion	39–41
Differential equation relating to average values in a canonical ensemble	42–44
This is identical in form with the fundamental differential equation of thermodynamics	44, 45

CHAPTER V.

AVERAGE VALUES IN A CANONICAL ENSEMBLE OF SYSTEMS.

Case of ν material points. Average value of kinetic energy of a single point for a given configuration or for the whole ensemble = $\frac{3}{2} \Theta$	46, 47
Average value of total kinetic energy for any given configuration or for the whole ensemble = $\frac{3}{2} \nu \Theta$	47
System of n degrees of freedom. Average value of kinetic energy, for any given configuration or for the whole ensemble = $\frac{n}{2} \Theta$	48–50
Second proof of the same proposition	50–52
Distribution of canonical ensemble in configuration	52–54
Ensembles canonically distributed in configuration	55
Ensembles canonically distributed in velocity	56

CHAPTER VI.

EXTENSION-IN-CONFIGURATION AND EXTENSION-IN-VELOCITY.

Extension-in-configuration and extension-in-velocity are invariants	57–59
---	-------

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

CONTENTS.

xv

	PAGE
Dimensions of these quantities	60
Index and coefficient of probability of configuration	61
Index and coefficient of probability of velocity	62
Dimensions of these coefficients	63
Relation between extension-in-configuration and extension-in-velocity	64
Definitions of extension-in-phase, extension-in-configuration, and extension-in-velocity, without explicit mention of coördinates	65-67

CHAPTER VII.

FARTHER DISCUSSION OF AVERAGES IN A CANONICAL ENSEMBLE OF SYSTEMS.

Second and third differential equations relating to average values in a canonical ensemble	68, 69
These are identical in form with thermodynamic equations enunciated by Clausius.	69
Average square of the anomaly of the energy — of the kinetic energy — of the potential energy	70-72
These anomalies are insensible to human observation and experience when the number of degrees of freedom of the system is very great	73, 74
Average values of powers of the energies	75-77
Average values of powers of the anomalies of the energies	77-80
Average values relating to forces exerted on external bodies	80-83
General formulæ relating to averages in a canonical ensemble	83-86

CHAPTER VIII.

ON CERTAIN IMPORTANT FUNCTIONS OF THE ENERGIES OF A SYSTEM.

Definitions. V = extension-in-phase below a limiting energy (ϵ). $\phi = \log dV/d\epsilon$	87, 88
V_q = extension-in-configuration below a limiting value of the potential energy (ϵ_q). $\phi_q = \log dV_q/d\epsilon_q$	89, 90
V_p = extension-in-velocity below a limiting value of the kinetic energy (ϵ_p). $\phi_p = \log dV_p/d\epsilon_p$	90, 91
Evaluation of V_p and ϕ_p	91-93
Average values of functions of the kinetic energy	94, 95
Calculation of V from V_q	95, 96
Approximate formulæ for large values of n	97, 98
Calculation of V or ϕ for whole system when given for parts	98
Geometrical illustration	99

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

xvi

CONTENTS.

CHAPTER IX.

THE FUNCTION ϕ AND THE CANONICAL DISTRIBUTION.

	PAGE
When $n > 2$, the most probable value of the energy in a canonical ensemble is determined by $d\phi/d\epsilon = 1/\Theta$	100, 101
When $n > 2$, the average value of $d\phi/d\epsilon$ in a canonical ensemble is $1/\Theta$	101
When n is large, the value of ϕ corresponding to $d\phi/d\epsilon = 1/\Theta$ (ϕ_0) is nearly equivalent (except for an additive constant) to the average index of probability taken negatively ($-\bar{\eta}$)	101–104
Approximate formulæ for $\phi_0 + \bar{\eta}$ when n is large	104–106
When n is large, the distribution of a canonical ensemble in energy follows approximately the law of errors	105
This is not peculiar to the canonical distribution	107, 108
Averages in a canonical ensemble	108–114

CHAPTER X.

ON A DISTRIBUTION IN PHASE CALLED MICROCANONICAL IN WHICH ALL THE SYSTEMS HAVE THE SAME ENERGY.

The microcanonical distribution defined as the limiting distribution obtained by various processes	115, 116
Average values in the microcanonical ensemble of functions of the kinetic and potential energies	117–120
If two quantities have the same average values in every microcanonical ensemble, they have the same average value in every canonical ensemble	120
Average values in the microcanonical ensemble of functions of the energies of parts of the system	121–123
Average values of functions of the kinetic energy of a part of the system	123, 124
Average values of the external forces in a microcanonical ensemble. Differential equation relating to these averages, having the form of the fundamental differential equation of thermodynamics	124–128

CHAPTER XI.

MAXIMUM AND MINIMUM PROPERTIES OF VARIOUS DISTRIBUTIONS IN PHASE.

Theorems I–VI. Minimum properties of certain distributions	129–133
Theorem VII. The average index of the whole system compared with the sum of the average indices of the parts	133–135

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

CONTENTS.

xvii

	PAGE
Theorem VIII. The average index of the whole ensemble compared with the average indices of parts of the ensemble . . .	135-137
Theorem IX. Effect on the average index of making the distribution-in-phase uniform within any limits	137-138

CHAPTER XII.

ON THE MOTION OF SYSTEMS AND ENSEMBLES OF SYSTEMS THROUGH LONG PERIODS OF TIME.

Under what conditions, and with what limitations, may we assume that a system will return in the course of time to its original phase, at least to any required degree of approximation? . . .	139-142
Tendency in an ensemble of isolated systems toward a state of statistical equilibrium	143-151

CHAPTER XIII.

EFFECT OF VARIOUS PROCESSES ON AN ENSEMBLE OF SYSTEMS.

Variation of the external coördinates can only cause a decrease in the average index of probability	152-154
This decrease may in general be diminished by diminishing the rapidity of the change in the external coördinates	154-157
The mutual action of two ensembles can only diminish the sum of their average indices of probability	158, 159
In the mutual action of two ensembles which are canonically distributed, that which has the greater modulus will lose energy . . .	160
Repeated action between any ensemble and others which are canonically distributed with the same modulus will tend to distribute the first-mentioned ensemble canonically with the same modulus . . .	161
Process analogous to a Carnot's cycle	162, 163
Analogous processes in thermodynamics	163, 164

CHAPTER XIV.

DISCUSSION OF THERMODYNAMIC ANALOGIES.

The finding in rational mechanics an <i>à priori</i> foundation for thermodynamics requires mechanical definitions of temperature and entropy. Conditions which the quantities thus defined must satisfy	165-167
The modulus of a canonical ensemble (Θ), and the average index of probability taken negatively ($\bar{\eta}$), as analogues of temperature and entropy	167-169

Cambridge University Press

978-1-108-01702-2 - Elementary Principles in Statistical Mechanics

Josiah Willard Gibbs

Frontmatter

[More information](#)

xviii

CONTENTS.

	PAGE
The functions of the energy $d\epsilon/d \log V$ and $\log V$ as analogues of temperature and entropy	169–172
The functions of the energy $d\epsilon/d\phi$ and ϕ as analogues of temperature and entropy	172–178
Merits of the different systems	178–183
If a system of a great number of degrees of freedom is microcanonically distributed in phase, any very small part of it may be regarded as canonically distributed	183
Units of Θ and $\bar{\eta}$ compared with those of temperature and entropy	183–186

CHAPTER XV.

SYSTEMS COMPOSED OF MOLECULES.

Generic and specific definitions of a phase	187–189
Statistical equilibrium with respect to phases generically defined and with respect to phases specifically defined	189
Grand ensembles, petit ensembles	189, 190
Grand ensemble canonically distributed	190–193
Ω must be finite	193
Equilibrium with respect to gain or loss of molecules	194–197
Average value of any quantity in grand ensemble canonically distributed	198
Differential equation identical in form with fundamental differential equation in thermodynamics	199, 200
Average value of number of any kind of molecules (ν)	201
Average value of $(\nu - \bar{\nu})^2$	201, 202
Comparison of indices	203–206
When the number of particles in a system is to be treated as variable, the average index of probability for phases generically defined corresponds to entropy	206