

CLASSICAL THEORETICAL PHYSICS



Greiner Neise Stöcker

THERMODYNAMICS
AND STATISTICAL
MECHANICS

热力学和统计力学

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Foreword

More than a generation of German-speaking students around the world have worked their way to an understanding and appreciation of the power and beauty of modern theoretical physics—with mathematics, the most fundamental of sciences—using Walter Greiner's textbooks as their guide.

The idea of developing a coherent, complete presentation of an entire field of science in a series of closely related textbooks is not a new one. Many older physicians remember with real pleasure their sense of adventure and discovery as they worked their ways through the classic series by Sommerfeld, by Planck and by Landau and Lifshitz. From the students' viewpoint, there are a great many obvious advantages to be gained through use of consistent notation, logical ordering of topics and coherence of presentation; beyond this, the complete coverage of the science provides a unique opportunity for the author to convey his personal enthusiasm and love for his subject.

These volumes on classical physics, finally available in English, complement Greiner's texts on quantum physics, most of which have been available to English-speaking audiences for some time. The complete set of books will thus provide a coherent view of physics that includes, in classical physics, thermodynamics and statistical mechanics, classical dynamics, electromagnetism, and general relativity; and in quantum physics, quantum mechanics, symmetries, relativistic quantum mechanics, quantum electro- and chromodynamics, and the gauge theory of weak interactions.

What makes Greiner's volumes of particular value to the student and professor alike is their completeness. Greiner avoids the all too common "it follows that. . ." which conceals several pages of mathematical manipulation and confounds the student. He does not hesitate to include experimental data to illuminate or illustrate a theoretical point and these data, like the theoretical content, have been kept up to date and topical through frequent revision and expansion of the lecture notes upon which these volumes are based.

Moreover, Greiner greatly increases the value of his presentation by including something like one hundred completely worked examples in each volume. Nothing is of greater importance to the student than seeing, in detail, how the theoretical concepts and tools under study are applied to actual problems of interest to a working physicist. And, finally, Greiner adds brief biographical sketches to each chapter covering the people responsible

for the development of the theoretical ideas and/or the experimental data presented. It was Auguste Comte (1789–1857) in his *Positive Philosophy* who noted, “To understand a science it is necessary to know its history.” This is all too often forgotten in modern physics teaching and the bridges that Greiner builds to the pioneering figures of our science upon whose work we build are welcome ones.

Greiner’s lectures, which underlie these volumes, are internationally noted for their clarity, their completeness and for the effort that he has devoted to making physics an integral whole; his enthusiasm for his sciences is contagious and shines through almost every page.

These volumes represent only a part of a unique and Herculean effort to make all of theoretical physics accessible to the interested student. Beyond that, they are of enormous value to the professional physicist and to all others working with quantum phenomena. Again and again the reader will find that, after dipping into a particular volume to review a specific topic, he will end up browsing, caught up by often fascinating new insights and developments with which he had not previously been familiar.

Having used a number of Greiner’s volumes in their original German in my teaching and research at Yale, I welcome these new and revised English translations and would recommend them enthusiastically to anyone searching for a coherent overview of physics.

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Preface

Thermodynamics and Statistical Mechanics contains the lectures that form part of the course in theoretical physics at the Johann Wolfgang Goethe-University in Frankfurt am Main. The lectures are given for students in physics in their fifth or sixth semester and are preceded by Theoretical Mechanics I (first semester), Theoretical Mechanics II (second semester), Classical Electrodynamics (third semester), Quantum Mechanics I (fourth semester), and Quantum Mechanics II—Symmetries and Relativistic Quantum Mechanics (fifth semester). Graduate course work, which begins with Quantum Mechanics II and Thermodynamics and Statistics, continues with Quantum Electrodynamics, the Gauge Theory of Weak Interactions, Quantum Chromodynamics, and other, more specialized courses in Nuclear and Solid State Theory, Cosmology, etc.

As in all other fields mentioned, we present thermodynamics and statistics according to the inductive method which comes closest to the methodology of the research physicist. Starting from some key experimental observations, the framework of the theory is developed and, after the basic equations are obtained, new phenomena are investigated from thereon.

The first part of the book covers basic thermodynamics with its wide range of applications in physics, chemistry and engineering. A large variety of examples and applications, as well as detailed descriptions of the necessary mathematical tools, are inserted to guide the reader through this vast field. Emphasis is laid on the microscopic understanding and interpretation of macroscopic processes. Among the subjects covered in this first part are the statistical interpretation of temperature and entropy (which is discussed in great detail, especially in the second part of this volume), thermodynamic machines, phase transitions and chemical reactions.

The second part deals with statistical mechanics. Microcanonical, canonical and macrocanonical ensembles are introduced and their various applications (ideal and real gases, fluctuations, paramagnetism and phase transitions) are demonstrated.

The third part covers quantum statistics. Beginning with ideal quantum gases, we discuss Fermi- and Bose gases and show their multiple applications which stretch from solid state physics to astrophysics (neutron stars and white dwarfs) and nuclear physics (nuclei, hadronic matter and the possible phase transition to a Quark Gluon Plasma).

The last part of this book presents a survey of real gases and phase transitions. Mayer's cluster expansion and the Ising- and Heisenberg- models serve as a basis for an introduction into this challenging new field of scientific research.

These lectures are now up for their third German edition. Over the years many students and collaborators have helped to work out exercises and illustrative examples. For this first English edition we enjoyed the enthusiastic input by Steffen A. Bass, Adrian Dumitru, Dirk Rischke (now at Columbia University) and Thomas Schönfeld. Miss Astrid Steidl drew the graphs and pictures. To all of them we express our sincere thanks. We are also grateful to Professor Jes Madsen of Aarhus University in Denmark and Professor Laszlo Csernai of the University Bergen in Norway for their valuable comments on the text and illustrations. We especially thank Professor Martin Gelfand from Colorado State University in Fort Collins and his group of students who collected numerous misprints and drew our attention to several physical problems.

Finally, we wish to thank Springer-Verlag New York, in particular Dr. Hans-Ulrich Daniel and Dr. Thomas von Foerster for their encouragement and patience, and Ms. Margaret Marynowski, for her expertise in copyediting the English edition.

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PART



THERMODYNAMICS

1 Equilibrium and State Quantities

Introduction

The theoretical description of systems consisting of very many particles is the center of interest in this volume of the series of lessons in *Theoretical Physics*. Such many-particle systems can be found everywhere in nature: on the one hand, e.g., the atoms and molecules in gases, fluids, solids or plasmas (with most of which one has daily experience) or on the other hand, the quantum gas of electrons in semiconductors or metals.

In burnt-out suns (white dwarfs) one finds the electron gas and nuclear matter (in the center of neutron stars and in supernova explosions), which consists of many neutrons and protons. Our universe was created in the “big bang” from a many-particle system of leptons, quarks and gluons.

In the following we will see that all these completely different systems obey common and very general physical laws. In particular, we will discuss the properties of such many-particle systems in thermodynamic equilibrium. Special emphasis will be laid on the microscopic point of view of statistical mechanics. Nevertheless, classical macroscopic thermodynamics shall not fall short, since it is of great importance: the concepts of thermodynamics are very general and to a great extent independent of special physical models, so that they are applicable in many fields of physics and the technical sciences.

The task of thermodynamics is to define appropriate physical quantities (the *state quantities*), which characterize macroscopic properties of matter, the so-called *macrostate*, in a way which is as unambiguous as possible, and to relate these quantities by means of universally valid equations (the *equations of state* and the *laws of thermodynamics*). Proceeding from daily experience one first sets up relations which seem to have general validity independent of the special physical system under consideration. These relations are the axiomatic laws of thermodynamics. Hence in the beginning, we have to define certain state quantities to formulate and substantiate the laws of thermodynamics, i.e., the energy law and the entropy law. These laws are, however, supplemented by a variety of empirically established relations between the state quantities (the equations of state), which are valid only for special physical systems. It is then sufficient to specify a few state quantities, called *state variables*, so that all other state quantities have certain uniquely

defined values. Thermodynamics cannot and will not give reasons why a certain equation of state describes a system. It restricts itself to making assertions concerning the state quantities, if a particular equation of state is given. It is already of great value to know that an equation of state exists at all (even if one cannot give it in explicit form), to explain certain general relationships.

However, the generality of thermodynamics, which is due to the fact that it is based on only a few empirical theorems, causes simultaneously a major restriction. The state quantities are phenomenologically defined by means of a prescription on how to measure them. Thermodynamics cannot make any assertions concerning reasons and interpretations on the microscopic level, which for the most part depend on a physical model. In particular, the very illustrative interpretation of the central concept of heat by means of the statistical, thermal motion of particles is not a subject of thermodynamics. Nevertheless, several times we will understand certain concepts only if we anticipate ideas pertaining to the microscopic regime. As already mentioned above, we are concerned with the equilibrium state. We will therefore precisely define this fundamental term and distinguish it from stationary or nonequilibrium states. Due to this restriction, equilibrium thermodynamics is not able to describe the temporal evolution of processes. However, it is possible, by a mere comparison of equilibrium states, to decide whether a process can happen or not. Here the concept of infinitesimal changes of state is extensively used. In thermodynamics one mostly deals with functions of more than one variable; hence we will often have to handle differentials and line integrals. We will not too much bother about mathematical rigor; rather we will try to gain insight into the physical fundamentals. Many students regard thermodynamics as very abstract and "dry." Hence we have included, as in the other volumes of this series, a variety of illustrative examples and problems, which shall illuminate the general notions of thermodynamics.

Systems, phases and state quantities

The concept of a thermodynamic system requires further specification. We define it to be an arbitrary amount of matter, the properties of which can be uniquely and completely described by specifying certain macroscopic parameters. The matter under consideration is confined by physical walls against the surroundings. If one makes further, special demands concerning these walls (i.e., the container), one distinguishes:

a. *Isolated systems*

These do not interact in any way with the surroundings. The container has to be impermeable to any form of energy or matter. Especially, the total energy E (mechanic, electric, etc.) is a conserved quantity for such a system and can thus be used to characterize the macrostate. The same holds for the particle number N and the volume V .

b. *Closed systems*

Here one allows only for the exchange of energy with the surroundings, but not for the exchange of matter. Thus, the energy is no longer a conserved quantity. Rather,

the actual energy of the system will fluctuate due to the energy exchange with the surroundings. However, if the closed system is in equilibrium with its surroundings, the energy will assume an average value which is related to the temperature of the system or of the surroundings. One can use the temperature, in addition to N and V , to characterize the macrostate.

c. *Open systems*

These systems can exchange energy and matter with their surroundings. Hence, neither the energy nor the particle number are conserved quantities. If the open system is in equilibrium with its surroundings, mean values of the energy and the particle number are assumed which are related to the temperature and the chemical potential (defined below). One can use the temperature and the chemical potential to characterize a macrostate.

It is obvious that at least the isolated system is an idealization, since in reality an exchange of energy with the surroundings cannot be prevented in the strict sense. However, by means of well-isolated vessels (dewars) isolated systems can be approximately realized.

If the properties of a system are the same for any part of it, one calls such a system *homogeneous*. However, if the properties change discontinuously at certain *marginal surfaces*, the system is *heterogeneous*. One calls the homogeneous parts of a heterogeneous system *phases* and the separating surfaces *phase boundaries*. A typical example for such a system is a closed pot containing water, steam and air. The phase boundary in this case is the surface of the water. One speaks of a gaseous phase (steam and air) and of a liquid phase (water). In some cases the macroscopic properties of a system depend on the size (and shape) of the phase boundaries. In our example, one has different macroscopic properties if the water covers the bottom of the pot or if it is distributed in the form of small drops (fog).

The macroscopic quantities which describe a system are called state quantities. Besides the energy E , the volume V , the particle number N , the entropy S , the temperature T , the pressure p and the chemical potential μ , such quantities include also the charge, the dipole momentum, the refractive index, the viscosity, the chemical composition and the size of phase boundaries. On the other hand, microscopic properties, e.g., the positions or momenta of the constituent particles, do not fall under the definition of state quantities. We will see later on (cf., the Gibbs phase rule) that the number of state quantities which are necessary for a unique determination of a thermodynamic state is closely related to the number of phases of a system. It is sufficient to choose a few state quantities (state variables), such that all other state quantities assume values which depend on the chosen state variables. The equations which in this way relate state quantities are called equations of state. The equations of state of a system have to be specified by empirical means. To this end one often uses polynomials of the state variables, the coefficients of which are then experimentally determined. It is important to realize that in most cases such empirical equations of state are in reasonable accordance with experiments only in a very limited range of values of the state variables. In particular, we refer in this context to the concept of the ideal gas, which one often uses as a model for real gases, but which allows for reliable assertions only in the limit of low density.

In general one distinguishes two classes of state quantities:

a. Extensive (additive) state quantities

These quantities are proportional to the amount of matter in a system, e.g., to the particle number or mass. Characteristic examples of extensive properties are the volume and the energy. In particular, an extensive state quantity of a heterogeneous system is *additively* composed of the corresponding extensive properties of the single phases. Thus, the volume of a pot containing water, steam and air is the sum of the volumes of the fluid and gaseous phases. The most characteristic extensive state quantity for thermodynamics (and statistical mechanics) is the entropy, which is closely related to the microscopic probability of a state.

b. Intensive state quantities

These quantities are independent of the amount of matter and are not additive for the particular phases of a system. They might assume different values in different phases, but this is not necessarily the case. Examples are: refractive index, density, pressure, temperature, etc. Typically, intensive state quantities can be defined locally; i.e., they may vary spatially. Consider, for instance, the density of the atmosphere, which is largest at the surface of the earth and continuously decreases with height, or the water pressure in an ocean, which increases with increasing depth.

For the moment, however, we will confine ourselves to spatially constant intensive properties. To determine the spatial dependences of intensive state variables requires additional equations (e.g., from hydrodynamics), or one has to use further equations of state (without exact knowledge about their origin). One often passes over from extensive state quantities to intensive state quantities which essentially describe very similar physical properties. For example, the energy, the volume and the particle number are extensive quantities, while the energy per unit volume (energy density) or the energy per particle, as well as the volume per particle, are intensive state quantities. Extensive variables change in proportion to the size of a system (if the intensive properties do not change and if we neglect surface effects), but this does not yield any new insight into the thermal properties of the system.

Equilibrium and temperature—the zeroth law of thermodynamics

Temperature is a state quantity which is unknown in mechanics and electrodynamics. It is specially introduced for thermodynamics, and its definition is closely connected with the concept of (thermal) equilibrium. *Equality of temperature* of two bodies is the condition for thermal equilibrium between these bodies. *Thermodynamic state quantities are defined (and measurable) only in equilibrium.*

Here the *equilibrium state* is defined as the one macroscopic state of a closed system which is automatically attained after a sufficiently long period of time such that the macroscopic state quantities no longer change with time. However, it requires some caution to use the notion of thermodynamic equilibrium for such a system. For example, it is not yet clear whether our universe is converging toward such an equilibrium state. Thus we