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# STATISTICAL PHYSICS

Second Edition

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**F. Mandl**

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Second Edition

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**F. Mandl**

*Department of Theoretical Physics,  
University of Manchester*

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# The Manchester Physics Series

*General Editors*

**F. MANDL   R. J. ELLISON   D. J. SANDIFORD**

*Physics Department, Faculty of Science,  
University of Manchester*

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# Editors' Preface to the Manchester Physics Series

The first book in the Manchester Physics Series, *Properties of Matter*, was published in 1970. Since then, eight volumes have appeared in the series and we have been extremely encouraged by the response of readers, both colleagues and students. These books have been reprinted many times and are being used world-wide in the English language edition and in translations. All the same, both the editors and authors feel the time is right for a revision of some of the books in order to take into account the feedback received and to reflect the changing style and needs of undergraduate courses.

The Manchester Physics Series is a series of textbooks on physics at undergraduate level. It grew out of our experience at Manchester University Physics Department, widely shared elsewhere, that many textbooks contain much more material than can be accommodated in a typical undergraduate course and that this material is only rarely so arranged as to allow the definition of a shorter self-contained course. In planning these books, we have had two objectives. One was to produce short books: so that lecturers should find them attractive for undergraduate courses; so that students should not be frightened off by their encyclopaedic size or their price. To achieve this, we have been very selective in the choice of topics, with the emphasis on the basic physics together with some instructive, stimulating and useful applications. Our second aim was to produce books which allow courses of different length and difficulty to be selected, with emphasis on different applications. To achieve such flexibility we have encouraged authors to use

flow diagrams showing the logical connections between different chapters and to put some topics in starred sections. These cover more advanced and alternative material which is not required for the understanding of later parts of each volume. Although these books were conceived as a series, each of them is self-contained and can be used independently of the others. Several of them are suitable for use outside physics courses; for example, *Electronics* is used by electronic engineers, *Properties of Matter* by chemists and metallurgists. Each author's preface gives details about the level, prerequisites, etc., of his volume.

We are extremely grateful to the many students and colleagues, at Manchester and elsewhere, whose helpful criticisms and stimulating comments have led to many improvements. Our particular thanks go to the authors for all the work they have done, for the many new ideas they have contributed, and for discussing patiently, and often accepting, our many suggestions and requests. We would also like to thank the publishers, John Wiley & Sons, who have been most helpful.

F. MANDL  
R. J. ELLISON  
D. J. SANDIFORD

January, 1987

# Preface to the Second Edition

My motivation for producing this second edition is to introduce two changes which, I believe, are substantial improvements.

First, I have decided to give much greater prominence to the Gibbs distribution. The importance of this formulation of statistical mechanics is due to its generality, allowing applications to a wide range of systems. Furthermore, the introduction of the Gibbs distribution as the natural generalization of the Boltzmann distribution to systems with variable particle numbers brings out the simplicity of its interpretation and leads directly to the chemical potential and its significance. In spite of its generality, the mathematics of the Gibbs approach is often much simpler than that of other approaches. In the first edition, I avoided the Gibbs distribution as far as possible. Fermi-Dirac and Bose-Einstein statistics were derived within the framework of the Boltzmann distribution. In this second edition, they are obtained much more simply taking the Gibbs distribution as the starting point. (For readers solely interested in the Fermi-Dirac and Bose-Einstein distributions, an alternative derivation, which does not depend on the Gibbs distribution, is given in section 11.3.) The shift in emphasis to the Gibbs approach has also led me to expand the section on chemical reactions, both as regards details and scope.

Secondly, I have completely revised the treatment of magnetic work in section 1.4, with some of the subtler points discussed in the new Appendix C. As is well known, the thermodynamic discussion of magnetic systems easily leads to misleading or even wrong statements, and I fear the first edition was not free from these. My new account is based on the work of two

colleagues of mine, Albert Hillel and Pat Buttle, and represents, I believe, an enlightening addition to the many existing treatments.

I have taken this opportunity to make some other minor changes: clarifying some arguments, updating some information and the bibliography, etc. Many of these points were brought to my attention by students, colleagues, correspondents and reviewers, and I would like to thank them all—too many to mention by name—for their help.

I would like to thank Henry Hall, Albert Hillel and Peter Lucas for reading the material on the Gibbs distribution, etc., and suggesting various improvements. I am most grateful to Albert Hillel and Pat Buttle for introducing me to their work on magnetic systems and for allowing me to use it, for many discussions and for helpful comments on my revised account. It is a pleasure to thank David Sandiford for his help throughout this revision, particularly for critically reading all new material, and Sandy Donnachie for encouraging me to carry out this work.

*January 1987*

FRANZ MANDL

# Preface to First Edition

This book is intended for an undergraduate course in statistical physics. The laws of statistical mechanics and thermodynamics form one of the most fascinating branches of physics. This book will, I hope, impart some of this fascination to the reader. I have discarded the historical approach of treating thermodynamics and statistical mechanics as separate disciplines in favour of an integrated development. This has some decisive advantages. Firstly, it leads more directly to a deeper understanding since the statistical nature of the thermodynamic laws, which is their true explanation, is put in the forefront from the very beginning. Secondly, this approach emphasizes the atomic nature of matter which makes it more stimulating and, being the mode of thought of most working physicists, is a more useful training. Thirdly, this approach is more economical on time, an important factor in view of the rapid expansion of science.

It is a consequence of this growth in scientific knowledge that an undergraduate physics course can no longer teach the whole of physics. There are many ways of selecting material. I have tried to produce a book which allows maximum flexibility in its use: to enable readers to proceed by the quickest route to a particular topic; to enable teachers to select courses differing in length, difficulty and choice of applications. This flexibility is achieved by means of the flow diagram (on the inside front cover) which shows the logical connections of the chapters. In addition, some sections are marked with a star ★ and some material, insufficient to justify a separate section, is printed on a tinted background. Material distinguished in either of these ways may be omitted. It is not needed later except very occasionally

in similarly marked parts, where explicit cross-references are always given.

My aim has been to explain critically the basic laws of statistical physics and to apply them to a wide range of interesting problems. A reader who has mastered this book should have no difficulties with one of the more advanced treatises or with tackling quite realistic problems. I have limited myself to systems in equilibrium, omitting irreversible thermodynamics, fluctuation phenomena and transport theory. This was partly for reasons of time and space, but largely because these topics are hardly appropriate for a fairly elementary account. For this reason also, I have not discussed the foundations of statistical physics but have based the theory on some simple intuitively plausible axioms. The ultimate justification of this approach lies in its success.

The development of statistical physics which I have given is self-contained, but the level of sophistication presupposes some previous acquaintance with the kinetic theory of gases, with the elementary descriptive ideas of atomic physics and with the rudiments of quantum theory. Fortunately, very little of the latter is required.

Over the past ten years I have given various undergraduate and post-graduate courses on statistical physics at Manchester University. In its present form, this book developed out of a course given to second-year undergraduates in physics, chemical physics and electronic engineering. This course of 26 lectures, of 50 minutes each, approximately covered the **unstarred** sections of the book, as well as the material of chapter 5 and of sections 7.5, 7.7, 11.4 and 11.5,\* omitting all material printed on tinted background. In addition, students were expected to solve about 20 problems. The answers were corrected, returned together with sample solutions, and discussed in class.

The problems and hints for solving them form an important part of the book. Attempting the problems and *then* studying the hints will **deepen** the reader's understanding and develop his skill and self-confidence in facing new situations. The problems contain much interesting physics which might well have found its way into the main body of the text.

This book was preceded by a preliminary edition which **was used** in my lecture course and was also distributed fairly widely outside Manchester University. I have received many comments and suggestions for **improvements and additions from readers**. I also had many stimulating discussions with students and colleagues at Manchester. As a result the original text has been greatly improved. I would like to thank all these people most warmly; there are too many of them to thank them all by name. However, I would

\*In the second edition, the numbers of these sections have become 11.5 and 11.6.

like to express my appreciation for their help to Professor Henry Hall and to Dr David Sandiford who read the whole manuscript and with whom I discussed difficult and obscure points until—temporarily at least—they seemed clear. Not only was this intellectual pursuit of great benefit to this book, but to me it was one of the joys of writing it.

*May, 1970*

F. MANDL

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Flow diagram

inside front cover

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\*Sections 11.1-11.2 and section 11.3 are alternative treatments which can be read independently of each other. Either suffices for the applications in sections 11.4 to 11.6. Sections 11.7 to 11.9 depend on section 11.1 only.

## CHAPTER

# 1

# The first law of thermodynamics

## 1.1 MACROSCOPIC PHYSICS

Statistical physics is devoted to the study of the physical properties of macroscopic systems, i.e. systems consisting of a very large number of atoms or molecules. A piece of copper weighing a few grams or a litre of air at atmospheric pressure and room temperature are examples of macroscopic systems. In general the number of particles in such a system will be of the order of magnitude of Avogadro's number  $N_0 = 6 \times 10^{23}$ . Even if one knows the law of interaction between the particles, the enormousness of Avogadro's number precludes handling a macroscopic system in the way in which one would treat a simple system—say planetary motion according to classical mechanics or the hydrogen molecule according to quantum mechanics. One can never obtain experimentally a complete microscopic\* specification of such a system, i.e. a knowledge of some  $10^{23}$  coordinates. Even if one were given this initial information, one would not be able to solve the equations of motion; some  $10^{23}$  of them!

In spite of the enormous complexity of macroscopic bodies when viewed from an atomistic viewpoint, one knows from everyday experience as well as from precision experiments that macroscopic bodies obey quite definite

\*'Microscopic' is here used in contrast to 'macroscopic'. It means a complete atomistic specification.

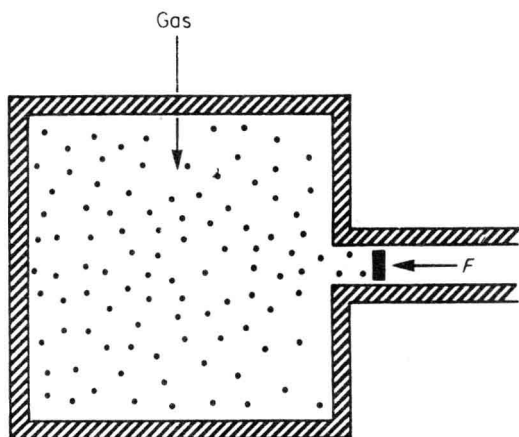


Fig. 1.1. Gas exerting pressure on movable piston, balanced by external applied force  $F$ .

laws. Thus when a hot and a cold body are put into thermal contact temperature equalization occurs; water at standard atmospheric pressure always boils at the same temperature (by definition called  $100^{\circ}\text{C}$ ); the pressure exerted by a dilute gas on a containing wall is given by the ideal gas laws. These examples illustrate that the laws of macroscopic bodies are quite different from those of mechanics or electromagnetic theory. They do not afford a complete microscopic description of a system (e.g. the position of each molecule of a gas at each instant of time). They provide certain macroscopic observable quantities, such as pressure or temperature. These represent averages over microscopic properties. Thus the macroscopic laws are of a statistical nature. But because of the enormous number of particles involved, the fluctuations which are an essential feature of a statistical theory turn out to be extremely small. In practice they can only be observed under very special conditions. In general they will be utterly negligible, and the statistical laws will in practice lead to statements of complete certainty.

To illustrate these ideas consider the pressure exerted by a gas on the walls of a containing vessel. We measure the pressure by means of a gauge attached to the vessel. We can think of this gauge as a freely movable piston to which a variable force  $F$  is applied, for example by means of a spring (Fig. 1.1). When the piston is at rest in equilibrium the force  $F$  balances the pressure  $P$  of the gas:  $P = F/A$  where  $A$  is the area of the piston.

In contrast to this macroscopic determination of pressure consider how the pressure actually comes about.\* According to the kinetic theory the

\*For a detailed derivation of the pressure of a perfect gas from kinetic theory, see Flowers and Mendoza,<sup>26</sup> section 5.1.2, R. Becker,<sup>2</sup> section 24, or Present,<sup>11</sup> Chapter 2.