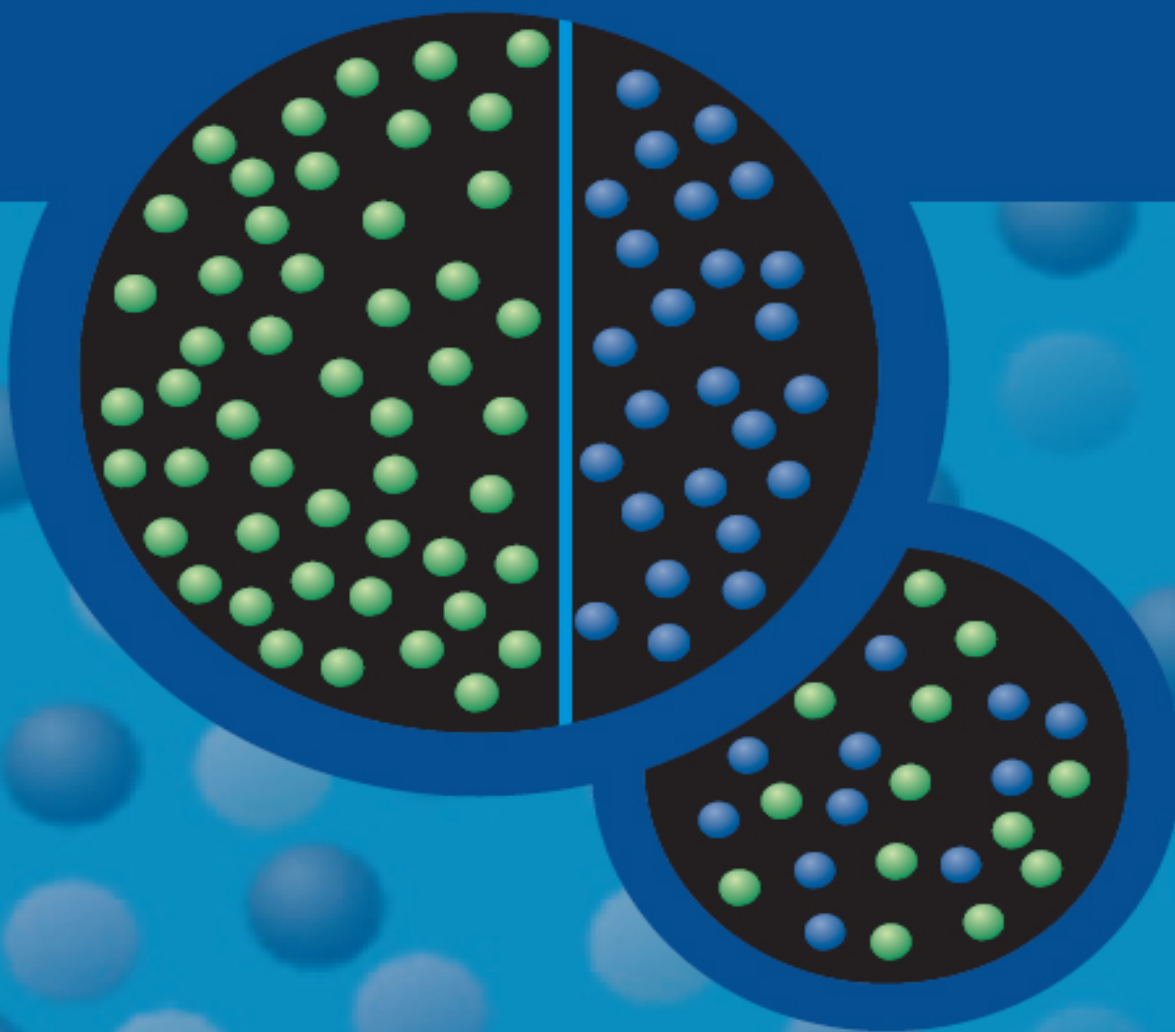


Statistical Physics

SECOND
EDITION

F. Mandl



 WILEY

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STATISTICAL PHYSICS

Second Edition

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THE MANCHESTER PHYSICS SERIES

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Editors' preface to the Manchester Physics Series

The Manchester Physics Series is a series of textbooks at first degree level. It grew out of our experience at the Department of Physics and Astronomy at Manchester University, 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 objective was to produce books which allow courses of different lengths 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 latter 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 wider use in other sciences. Each Author's Preface gives details about the level, prerequisites, etc., of his volume.

The Manchester Physics Series has been very successful with total sales of more than a quarter of a million copies.

We are extremely grateful to the many students and colleagues, at Manchester and elsewhere, for helpful criticisms and stimulating comments. 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, the suggestions of the editors.

Finally, we would like to thank our publishers, John Wiley & Sons Ltd, for their enthusiastic and continued commitment to the Manchester Physics Series.

D. J. Sandiford
F. Mandl
A. C. Phillips
February 1997

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 postgraduate 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 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

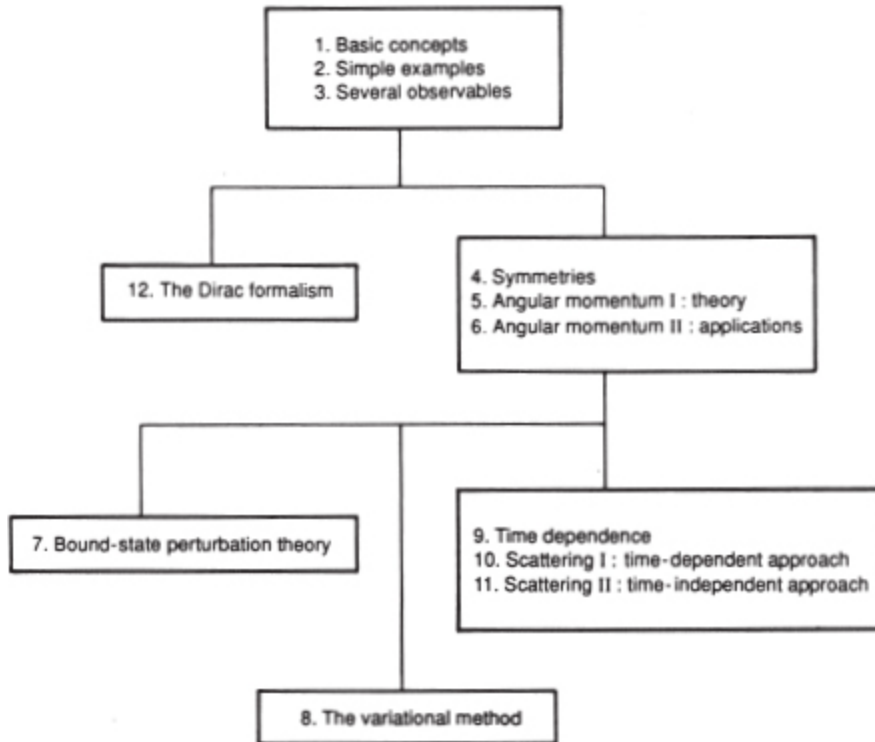
only was this intellectual pursuit of great benefit to this book, but to me it was one of the joys of writing it.

May, 1970

F. MANDL

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

FLOW DIAGRAM



Each chapter presupposes material only from chapters on the downward path leading to it.

Physical Constants

<i>Constant</i>	<i>Value</i>	<i>Symbol</i>
Avogadro's number	$6.02 \times 10^{23} \text{ mol}^{-1}$	N_o
Boltzmann's constant	$\begin{cases} 1.381 \times 10^{-23} \text{ J K}^{-1} \\ 8.62 \times 10^{-5} \text{ eV K}^{-1} \end{cases}$	k
gas constant	$\begin{cases} 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \\ 1.99 \text{ cal mol}^{-1} \text{ K}^{-1} \end{cases}$	R
molar volume at STP	$22.4 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$	
Planck's constant	$6.626 \times 10^{-34} \text{ J s}$	h
(Planck's constant)/ 2π	$\begin{cases} 1.055 \times 10^{-34} \text{ J s} \\ 6.58 \times 10^{-16} \text{ eV s} \end{cases}$	\hbar
velocity of light	$3 \times 10^{10} \text{ cm s}^{-1}$	c
charge of the proton	$\begin{cases} 1.60 \times 10^{-19} \text{ C} \\ 4.80 \times 10^{-10} \text{ esu} \end{cases}$	e
Bohr radius	$0.529 \times 10^{-8} \text{ cm}$	a_o
electron rest mass	$\begin{cases} 9.11 \times 10^{-28} \text{ g} \\ 0.511 \text{ MeV} \end{cases}$	m_e
proton rest mass	$\begin{cases} 1.67 \times 10^{-24} \text{ g} \\ 938 \text{ MeV} \end{cases}$	m_p
Bohr magneton	$\begin{cases} e\hbar/2m_e & 9.27 \times 10^{-24} \text{ A m}^2 \\ e\hbar/2m_e c & 9.27 \times 10^{-21} \text{ erg G}^{-1} \end{cases}$	μ_B
nuclear magneton $\mu_N(m_e/m_p)$	$\begin{cases} 5.05 \times 10^{-27} \text{ A m}^2 \\ 5.05 \times 10^{-24} \text{ erg G}^{-1} \end{cases}$	μ_N
temperature of the ice point	273.15 K	T_{ice}

CHAPTER 1

The first law of thermodynamics

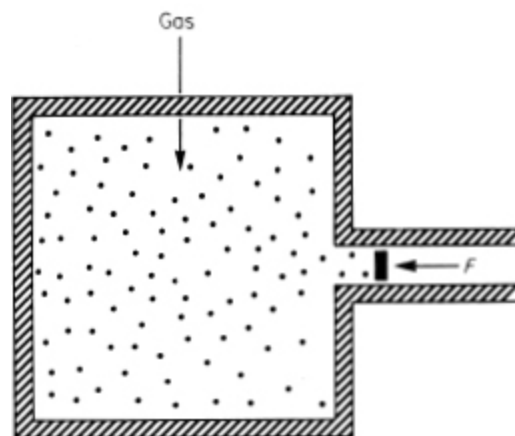
1.1 MACROSCOPIC PHYSICS

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 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 °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.

[Fig. 1.1](#). Gas exerting pressure on movable piston, balanced by external applied force F .



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 molecules of the gas are undergoing elastic collisions with the walls. The pressure due to these collisions is certainly not a strictly constant time-independent quantity. On the contrary the instantaneous force acting on the piston is a rapidly fluctuating quantity. By the pressure of the gas we mean the average of this fluctuating force over a time interval sufficiently long for many collisions to have occurred in this time. We may then use the steady-state velocity distribution of the molecules to calculate the momentum transfer per unit area per unit time from the molecules to the wall, i.e. the pressure. The applied force F acting on the piston can of course only approximately balance these irregular impulses due to molecular collisions. On average the piston is at rest but it will perform small irregular vibrations about its equilibrium position as a consequence of the individual molecular collisions. These small irregular movements are known as Brownian motion (Flowers and Mendoza,²⁶ section 4.4.2). In the case of our piston, and generally, these minute movements are totally unobservable. It is only with very small macroscopic bodies (such as tiny particles suspended in a liquid) or very sensitive apparatus (such as the very delicate suspension of a galvanometer — see section 7.9.1) that Brownian motion can be observed. It represents one of the ultimate limitations on the accuracy of measurements that can be achieved.

There are two approaches to the study of macroscopic physics. Historically the oldest approach, developed mainly in the first half of the 19th century by such men as Carnot, Clausius, William Thomson (the later Lord Kelvin), Robert Mayer and Joule, is that of classical thermodynamics. This is based on a small number of basic principles—the laws of thermodynamics—which are deductions from and generalizations of a large body of experiments on macroscopic systems. They are phenomenological laws, justified by their success in describing macroscopic phenomena. They are not derived from a microscopic picture but avoid all atomic concepts and operate exclusively with macroscopic variables, such as pressure, volume, temperature, describing the properties of systems in terms of these. Of course, the avoidance of atomic concepts severely limits the information that thermodynamics can provide about a system. In particular, the equation of state (e.g. for an ideal gas: $PV=RT$) which relates the macroscopic variables and which distinguishes one system from another must be derived from experiment. But there are many situations where a microscopic description is not necessary or not practicable and where thermodynamics proves its power to make far-reaching deductions of great generality.*

The second approach to macroscopic physics is that of statistical mechanics. This starts from the atomic constitution of matter and endeavours to derive the laws of macroscopic bodies from the atomic properties. This line of approach originated in Maxwell's kinetic theory of gases which led to the profound works of Boltzmann and of Gibbs. There are two aspects to statistical mechanics. One aim is to *derive* the thermodynamic laws of macroscopic bodies from the laws governing their atomic behaviour. This is a fascinating but very difficult field. Nowadays one has a fairly general understanding of the underlying physics but most

physicists working in the field would probably agree that no real proofs exist. In this book we shall not consider these aspects of statistical mechanics and shall only give arguments which make the thermodynamic laws plausible from the microscopic viewpoint.

The second objective of statistical mechanics is to derive the properties of a macroscopic system — for example, its equation of state — from its microscopic properties. Essentially this is done by averaging over unobservable microscopic coordinates leaving only macroscopic coordinates such as the volume of a body, as well as other macroscopic variables, such as temperature or specific heat, which have no counterpart in mechanics and which represent averages over unobservable microscopic coordinates.

This division of macroscopic physics into thermodynamics and statistical mechanics is largely of historical origin. We shall not follow this development. Instead we shall emphasize the unity of the subject, showing how the two aspects illuminate each other, and we shall use whichever is more appropriate.

1.2 SOME THERMAL CONCEPTS

Some of the variables which were introduced in the last section to describe a macroscopic system, such as its volume or pressure, have a direct meaning in terms of mechanical concepts, e.g. one can measure the pressure of gas in a container by means of a mercury manometer. However, some of the concepts are quite foreign to mechanics. Of these the one most basic to the whole of statistical thermodynamics is that of temperature. Originally temperature is related to the sensations of 'hot' and 'cold'.

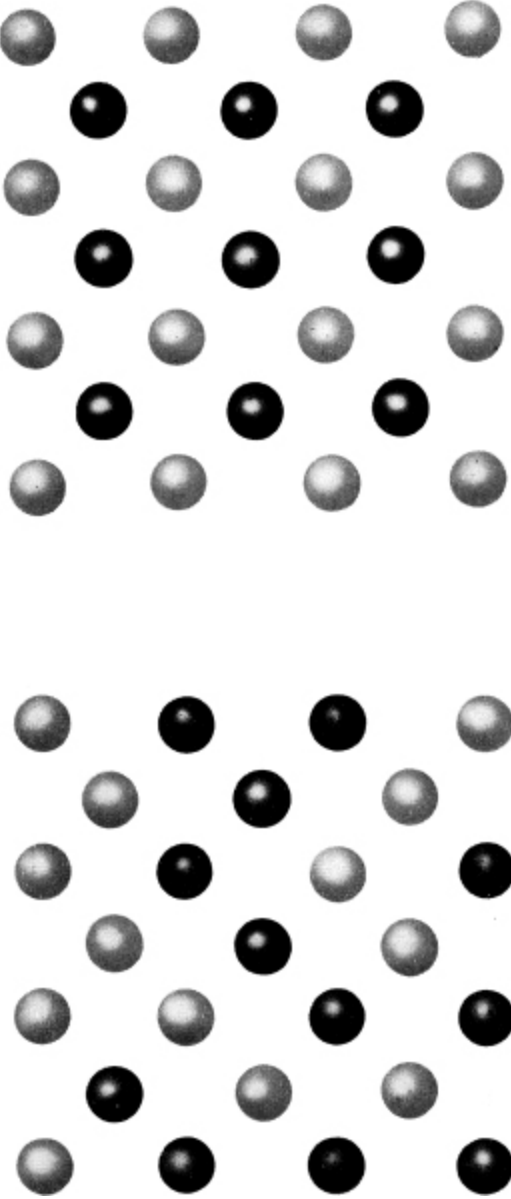
The most remarkable feature of temperature is its tendency to equalization: i.e. if a hot and a cold body are put into thermal contact, the hot body cools down and the cold body warms up until both bodies are at the same temperature. This equalization is due to a net flow of energy from the hotter to the colder body. Such a flow of energy is called a flow of heat. When this flow of heat ceases, the two bodies are in thermal equilibrium. The basic fact of experience which enables one to compare the temperatures of two bodies by means of a third body is that if two bodies are each in thermal equilibrium with a third body they are also in thermal equilibrium with each other. This statement is sometimes referred to as the zeroth law of thermodynamics. To measure temperature, one can utilize any convenient property of matter which depends on its degree of hotness, such as the electric resistance of a platinum wire, the volume (i.e. length in a glass capillary) of a mass of mercury, the pressure of a given mass of gas contained in a fixed volume. For each of these thermometers one can then define a Celsius (centigrade) scale by calling the temperatures of the ice and steam points* 0 °C and 100 °C and interpolating linearly for other temperatures. It turns out that these different temperature scales do not agree exactly (except at the fixed points, of course). They depend on the particular thermometer used. We shall see presently that this arbitrariness is removed by the second law of thermodynamics which enables one to define an *absolute temperature scale*, i.e. one which is independent of the experimental arrangement used for measuring the temperature. The physical meaning of the absolute temperature is revealed by statistical mechanics. It turns out to be a measure of the energy associated with the molecular, macroscopically unobserved, motions of a system.

Above we considered temperature equilibrium. More generally, let us consider an isolated system. This system may be in a state containing all sorts of pressure differences, temperature gradients, inhomogeneities of density, concentrations, etc. A system in such a state is of course not in equilibrium. It will change with time as such processes as pressure equalization, thermal conduction, diffusion, etc., occur. Left to itself, the system eventually reaches a state in which all these pressure gradients, etc., have disappeared and the system undergoes no further macroscopically observable changes. We call such a state an *equilibrium state*. Of course, this is not static equilibrium. Sufficiently refined experiments will show up the thermal motions, a typical example being Brownian motion. The time that a system requires to reach equilibrium depends on the processes involved. In general there will be several mechanisms, as we have seen; each will possess its own characteristic relaxation time. After a time long compared to all relaxation times the system will be in equilibrium.

On the other hand there are frequently situations where the relaxation time for a particular process is very long compared with the time for which a system is observed. One can then ignore this process altogether. It occurs too slowly to be of any consequence. In many cases the relaxation time is for practical purposes infinite. Consider a binary alloy, for example β -brass which consists of Cu and Zn atoms in equal numbers. At sufficiently low temperatures, the stable equilibrium configuration of the atoms is one where they are ordered in a regular mosaic-like pattern in the crystal lattice. No such ordering occurs at high temperatures. The two situations are schematically illustrated for a two-dimensional model lattice in [Figs. 1.2\(a\)](#) and [\(b\)](#). If such an alloy is rapidly cooled from a high to a low temperature, the atoms get 'frozen' into their instantaneous disordered pattern. This is a metastable state

but the rate of migration of the atoms at the low temperature is so small that for practical purposes the disorder will persist for all times.

[Fig. 1.2.](#) Schematic two-dimensional model of a binary alloy: (a) in ordered state, (b) in disordered state.



In β -brass the Cu and Zn atoms each form a simple cubic lattice, the two lattices being interlocked so that each Cu atom is at the centre of a cube formed by 8 Zn atoms, and vice versa. There is an attractive force between the Cu and Zn atoms. At low temperatures this attraction dominates over the comparatively feeble thermal motion resulting in an ordered state, but at high temperatures the thermal agitation wins. The ordering shows up as extra diffraction lines in x-ray diffraction, since the two types of atom will scatter x-rays differently.

We have discussed relaxation times in order to explain what is meant by equilibrium. The calculation of how long it takes for equilibrium to establish itself, and of non-equilibrium processes generally, is extremely difficult. We shall not consider such questions in this book but shall exclusively study the properties of systems in equilibrium without inquiring how they reached equilibrium. But we shall of course require a criterion for characterizing an equilibrium state. The second law of thermodynamics provides just such a criterion.

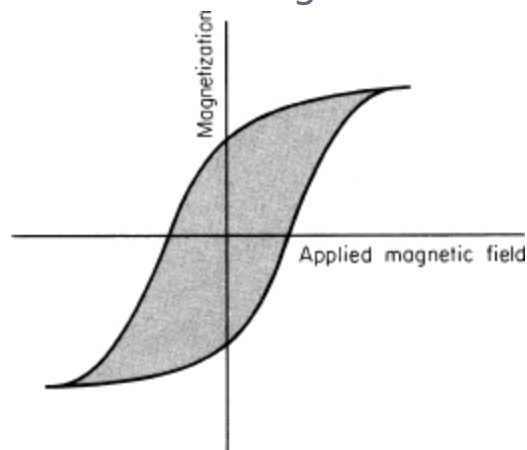
The description of a system is particularly simple for equilibrium states. Thus for a fluid not in equilibrium it may be necessary to specify its density at every point in space as a function of time, whereas for equilibrium the density is uniform and constant in time. The equilibrium state of a system is fully determined by a few macroscopic variables. These variables then determine all other macroscopic properties of the system. Such properties which depend only on the state of a system are called *functions of state*. The state of a homogeneous fluid is fully determined by its mass M , volume V , and pressure P . Its temperature T is then a function of state determined by these, i.e.

$$(1.1) \quad T=f(P, V, M) .$$

[Eq. \(1.1\)](#) is called the equation of state of the fluid. Of course, we could have chosen other independent variables to specify the state of the fluid, for example M , V and T , and found P from [Eq. \(1.1\)](#).

In our discussion of a fluid we tacitly assumed the characteristic property of a fluid: that its thermodynamic properties are independent of its shape. This makes a fluid a very simple system to discuss. More complicated systems require a larger number of parameters to determine a unique state and lead to a more complicated equation of state. This mode of description of a system breaks down if its state depends not only on the instantaneous values of certain parameters but also on its previous history, i.e. in the case of hysteresis effects such as occur in ferromagnetic materials or the plastic deformation of solids. In the former example the magnetization is not a unique function of the applied magnetic field ([Fig. 1.3](#)); in the latter, the strain is not a unique function of the applied stress ([Fig. 1.4](#)).*

[Fig. 1.3.](#) Hysteresis in a ferromagnetic material.



[Fig. 1.4.](#) Stress-strain relationship in a solid showing the hysteresis loop.