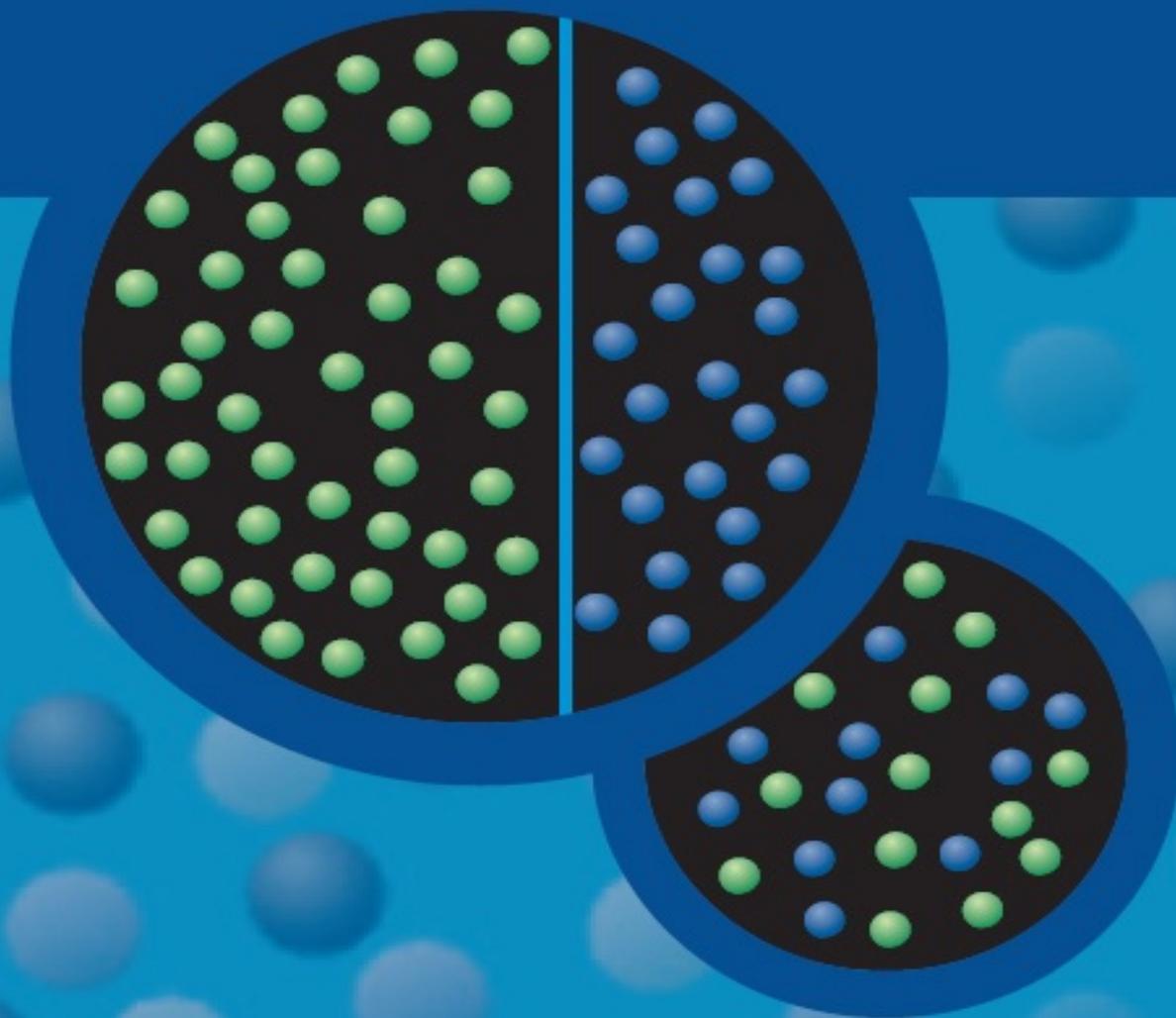


# Statistical Physics

SECOND  
EDITION

F. Mandl



 WILEY

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# STATISTICAL PHYSICS

Second Edition

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**F. Mandl**

*Department of Theoretical Physics,  
University of Manchester*

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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. The books 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 them 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. Manly  
A. C. Phillips  
*February 1995*

# Preface to the Second Edition

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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 the 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 of emphasis to the Gibbs approach has also led me to expand the section on chemical reactions, both in 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 Sandie Donnachie for encouraging me to carry out this work.

*January 1987*

FRANZ MANDL

# Preface to First Edition

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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 20 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.

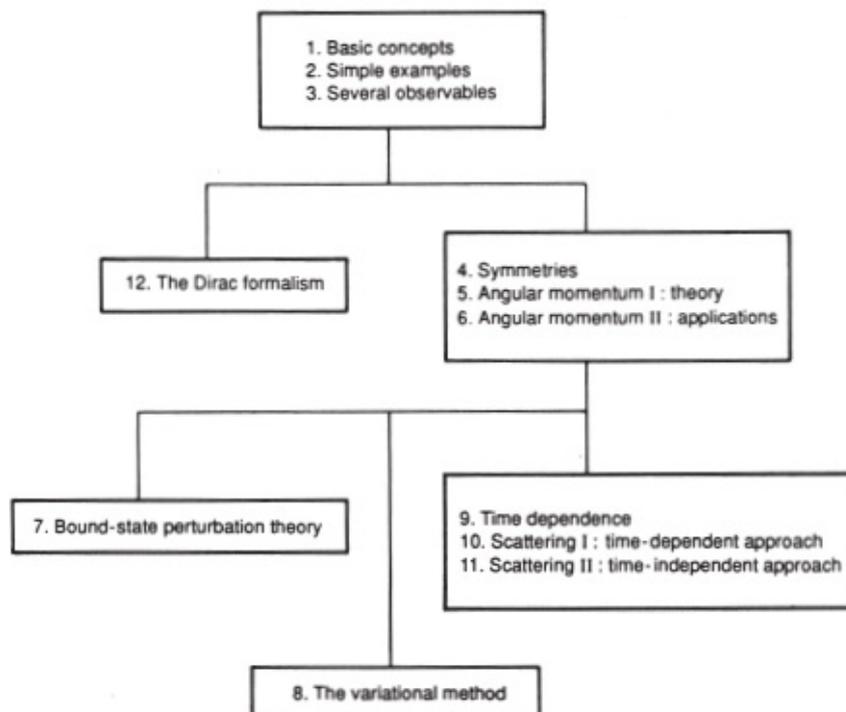
~~This book was preceded by a preliminary edition which was used in my lecture course and was also distributed fairly widely outside Manchester University. I have received many comments and suggestions for improvements and additions from readers. I also had many stimulating discussions with students 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 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. MANDERSON

\*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)/ $2\pi$	$\begin{cases} 1.055 \times 10^{-34} \text{ J s} \\ 6.58 \times 10^{-16} \text{ eV s} \end{cases}$	$\hbar$
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	$\begin{cases} e\hbar/2m_e & 9.27 \times 10^{-24} \text{ A m}^2 \\ e\hbar/2m_e c & 9.27 \times 10^{-21} \text{ erg G}^{-1} \end{cases}$	$\mu_B$
nuclear magneton $\mu_B(m_e/m_p)$	$\begin{cases} 5.05 \times 10^{-27} \text{ A m}^2 \\ 5.05 \times 10^{-24} \text{ erg G}^{-1} \end{cases}$	$\mu_N$
temperature of the ice point	$273.15 \text{ K}$	$T_{ice}$



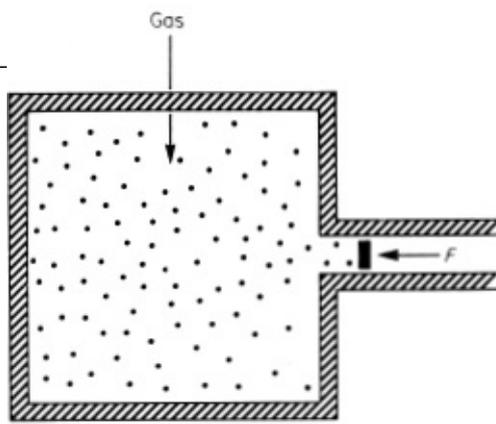
## The first law of thermodynamics

### 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 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 atomist 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. They 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,<sup>26</sup> 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. This 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

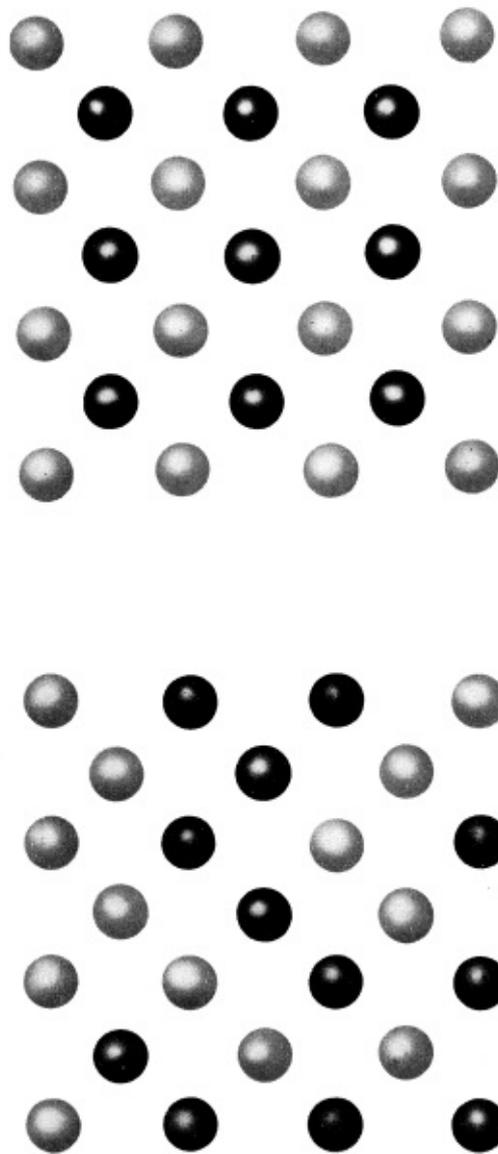
Some of the variables which were introduced in the last section to describe a macroscopic system, such as its volume or pressure, have a direct meaning in terms of mechanical concepts, e.g. one can measure the pressure of gas in a container by means of a mercury manometer. However, some of the concepts 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 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 electrical 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  $0^\circ\text{C}$  and  $100^\circ\text{C}$  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

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  $\beta$ -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  $\beta$ -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 reach 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.

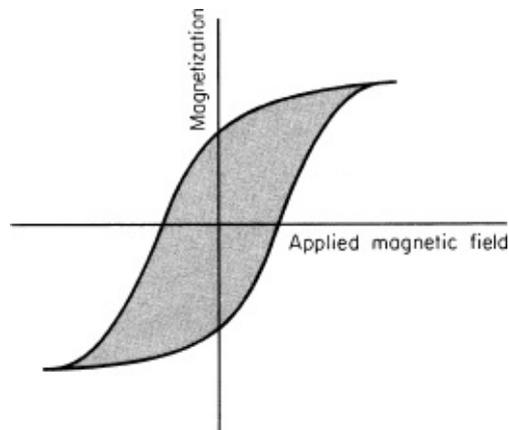
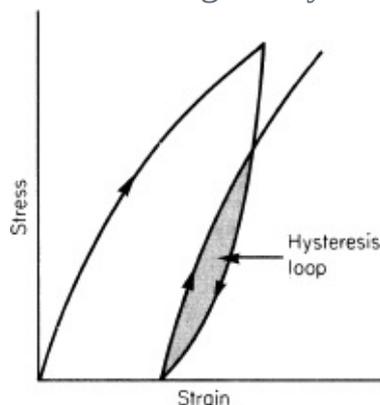


Fig. 1.4. Stress-strain relationship in a solid showing the hysteresis loop.



In general the equation of state of a substance is very complicated. It must be found from experiment and does not allow a simple analytic representation. The perfect (or ideal) gas is an exception. For real gases, at sufficiently low pressures, the pressure and volume of a fixed mass of gas are very nearly related by

$$(1.2) \quad PV = \text{const.}$$

at a given temperature. An equation such as (1.2), relating different states of a system, all at the same temperature, is called an *isotherm*. A perfect gas is defined to be a fluid for which the relation (1.2) holds *exactly* for an isotherm, i.e. a perfect gas represents an extrapolation to zero pressure from real

gases. We can use this to define a (perfect) gas temperature scale  $T$  by the relation

$$(1.3) \quad T \propto \lim_{P \rightarrow 0} PV .$$

The gas temperature scale is then completely determined if we fix *one* point on it by *definition*. The point is taken as the triple point of water, i.e. the temperature at which ice, water and water vapor coexist in equilibrium. The reason for this choice is that the triple point corresponds to a unique temperature and pressure of the system (see section 8.3). The triple point temperature  $T_{tr}$  was chosen so that the size of the degree on the gas scale equals as nearly as possible the degree Celsius, i.e. according to the best available measurements there should be a temperature difference of 100 degrees between the steam and ice points. This criterion led to

$$(1.4) \quad T_{tr} = 273.16 \text{ K}$$

being internationally adopted in 1954 as the *definition* of the triple point. (Very accurate measurements, in the future, of the steam and ice points on this temperature scale may result in the temperature difference being not *exactly* 100 degrees.) In Eq. (1.4) we have written K (kelvin) in anticipation of the fact that the gas scale will turn out to be identical with the absolute thermodynamic temperature scale. (Older notations for K are deg. or °K.) Any other absolute temperature is then, in principle, determined from Eqs. (1.3) and (1.4). The temperature of the ice point becomes 273.15 K.

The constant of proportionality, still missing in Eq. (1.3), is determined from accurate measurements with gas thermometers. For one mole (we shall always use the gram-mole) of gas one finds that

$$(1.5) \quad PV = RT$$

with the gas constant  $R$  having the value

$$(1.6) \quad R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} .$$

From Avogadro's number

$$(1.7) \quad N_0 = 6.02 \times 10^{23} \text{ molecules/mole} ,$$

we can calculate Boltzmann's constant  $k$ , i.e. the gas constant per molecule

$$(1.8) \quad k = R/N_0 = 1.38 \times 10^{-23} \text{ J/K} .$$

The equation of state of a perfect gas consisting of  $N$  molecules can then be written

$$(1.9) \quad PV = NkT .$$

The physically significant quantity in this equation is the energy  $kT$ . Under classical conditions, i.e. when the theorem of equipartition of energy holds (see, for example, section 7.9.1 below, or Flowers and Mendoza,<sup>26</sup> sections 5.3 and 5.4.4),  $kT$  is of the order of the energy of one molecule in a macroscopic body at temperature  $T$ . By contrast, Boltzmann's Constant is merely a measure of the size of the degree Celsius. At  $T = 290\text{K}$  (room temperature)

$$(1.10) \quad kT = 4.0 \times 10^{-21} \text{ J} = \frac{1}{40} \text{ eV}$$

where we introduced the electron-volt (eV):

$$(1.11) \quad \begin{aligned} 1 \text{ eV} &= 1.60 \times 10^{-19} \text{ J} \\ &= 1.60 \times 10^{-12} \text{ erg} . \end{aligned}$$

The electron-volt is a reasonably-sized unit of energy on the atomic scale. For example, the ionization

energy of atoms varies from about 4 eV to about 24 eV; the cohesive energy of solids varies from about 0.1 eV to about 10 eV per molecule, depending on the type of binding force.

## 1.3 THE FIRST LAW

We shall now consider the application of the universally valid principle of conservation of energy to macroscopic bodies. The new feature, which makes this different from merely a very complicated problem in mechanics, is that we do not want to describe the system on the microscopic scale, i.e. in terms of the individual molecular motions. This is of course impossibly complicated. Instead we want to describe the motion associated with these internal degrees of freedom in terms of macroscopic parameters.

Consider a system enclosed in walls impervious to heat transmission. Such walls are called adiabatic walls. (In practice one uses a dewar flask to obtain these conditions.) We can change the state of such a thermally isolated system by doing work on it. There is overwhelming experimental evidence that for a change from a definite state 1 to another definite state 2 of the system the same amount of work  $W$  is required irrespective of the mechanism used to perform the work or the intermediate states through which the system passes. Historically the earliest precise evidence comes from Joule's work, published in 1843, on the mechanical equivalent of heat. He produced given changes of state in a thermally isolated liquid in different ways. These included vigorously stirring the liquid with a paddle-wheel driven by weights (Fig. 1.5) and supplying electrical work by inserting a resistor carrying a current in the liquid (Fig. 1.6). The work done on the system — known in the first case from the motion of the weights, in the second from the current through the resistor and the potential drop across it — is the same in both cases.

We can hence define a *function of state*  $E$ , such that for a change from a state 1 to a state 2 of a *thermally isolated system* the work done on the system equals the change in  $E$ :

$$(1.12) \quad W = \Delta E \equiv E_2 - E_1 .$$

$E$  is called the energy of the system. Except for an arbitrary choice of the zero of the energy scale (i.e. of the energy of a standard reference state) Eq. (1.12) determines the energy of any other state.

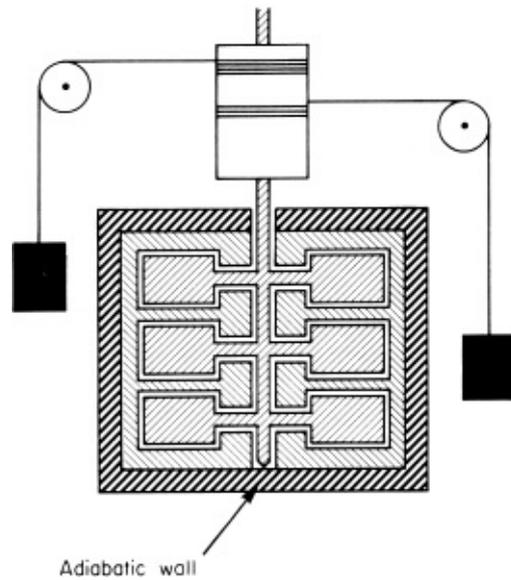
Suppose we now consider changes of state of the system no longer thermally isolated. It turns out that we can in general still effect the same change from state 1 to state 2 of the system but in general the work  $W$  done on the system does not equal the increase in energy  $\Delta E$  of the system. We define the deficit

$$(1.13) \quad Q = \Delta E - W$$

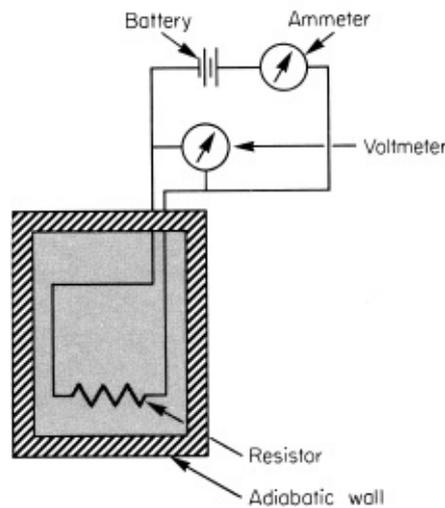
as the heat supplied to the system. Eq. (1.13) is the general statement of the first law of thermodynamics. It is the law of conservation of energy applied to processes involving macroscopic bodies. The concept of heat, as introduced here, has all the properties associated with it from calorimetry experiments, etc. These are processes in which no work is done, the temperature change being entirely due to heat transfer.

Let us consider how the energy  $E$  of a given state of a macroscopic system subdivides. (For definiteness you might think of the system as a gas or a crystal.) According to the laws of mechanics the energy  $E$  is the sum of two contributions: (i) the energy of the macroscopic mass motion of the system, (ii) the internal energy of the system.

[Fig. 1.5.](#) Schematic picture of Joule's paddle-wheel experiment. A system for doing mechanical work on the liquid in the calorimeter.



[Fig. 1.6.](#) A system for doing electrical work on the liquid in the calorimeter.



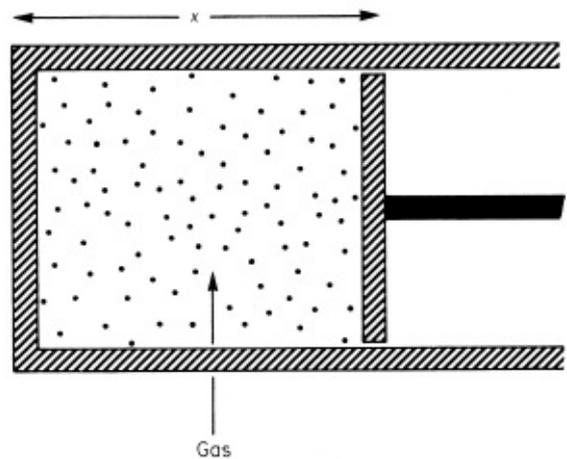
The energy of the mass motion consists of the kinetic energy of the motion of the centre of mass of the system, plus any potential energy which the system might possess due to the presence of an external field of force. For example, the system might be in a gravitational field. In statistical physics one is usually interested in the internal properties of systems, not in their macroscopic mass motion. Usually we shall be considering systems at rest and the potential energy of any external fields will be unimportant so that we shall not distinguish between the energy and the internal energy of a system.

The internal energy of a system is the energy associated with its internal degrees of freedom. It is the kinetic energy of the molecular motion (in a frame of reference in which the system is at rest) plus the potential energy of interaction of the molecules with each other. In an ideal gas at rest the internal energy is the sum of the kinetic energies of the translational motions of the molecules plus the internal energies of the molecules due to their rotations, etc. In a crystal the internal energy consists of the kinetic and potential energies of the atoms vibrating about their equilibrium positions in the crystal lattice. Thus the internal energy is the energy associated with the 'random' molecular motion of the system. We shall see later that the temperature of a system is a measure of its internal energy, which is therefore also called the thermal energy of the system.

The internal energy of a system is a function of state. For a fluid we could write  $E = E(P, T)$  or  $E = E(V, T)$ , depending on which independent variables we choose to specify the state of the fluid. (W

have suppressed the dependence on the mass of the fluid in these expressions for  $E$  as we shall usually be considering a constant mass, i.e. size of system, and are only interested in the variation of the other variables. In most cases the dependence on the size is trivial.) Thus for the change of a system from state 1 to a state 2,  $\Delta E$  in Eq. (1.13) is the difference of two energies,  $E_1$  and  $E_2$ , for these two states given by Eq. (1.12). By contrast  $Q$  and  $W$  are *not* changes in functions of state. There exists *no* function of state ‘heat of a system’ such that the system has a definite ‘heat’ in state 1 and a definite ‘heat’ in state 2, with  $Q$  the difference of these ‘heats’. Similarly there exists *no* function of state ‘work of a system’ such that the system has a definite ‘work’ in state 1 and a definite ‘work’ in state 2 with the difference of these ‘works’. It follows that there is no conservation of ‘heat’ by itself, no conservation of ‘work’ by itself. We only have conservation of energy, given by Eq. (1.13). *Work and heat flow are different forms of energy transfer.* The physical distinction between these two modes is that work is energy transfer via the macroscopically observable degrees of freedom of a system whereas heat flow is the direct energy transfer between microscopic, i.e. internal, degrees of freedom. For examples of these two modes of energy transfer we again consider a gas. If the gas is contained in a thermally isolated cylinder, closed off at one end by a movable piston (Fig. 1.7), then work can be done on the gas by compressing it. The macroscopic degree of freedom here corresponds to the position coordinate  $x$  of the piston. During the compression the gas is warmed up. From the molecular standpoint this warming up comes about because in elastic collisions with the moving piston the molecules gain energy which, as a result of subsequent collisions between molecules, is shared by all of them. Next assume that the gas is contained in a vessel with fixed walls and that there exists a temperature gradient in the gas. If we consider an element of area normal to this gradient, then a net transport of energy occurs across this area. This is the process of thermal conduction in the gas. Its explanation on the molecular scale is that molecules traversing this element of area from opposite sides possess different kinetic energies on average, corresponding to the different temperatures which exist in the regions from which those molecules came (for details, see Flowers and Mendoza, Chapter 6, or Present,<sup>11</sup> Chapter 3).

Fig. 1.7. Adiabatic compression of a gas.



Eq. (1.13) expresses the conservation of energy for finite changes. For infinitesimal changes we correspondingly write

$$(1.14) \quad dE = dQ + dW .$$

Here  $dE$  is the infinitesimal change in the energy of the system, brought about by an infinitesimal amount of work  $dW$  and an infinitesimal heat transfer  $dQ$ . We write  $dW$  and  $dQ$  (not  $dW$  and  $dQ$ ) to emphasize that, as discussed, these infinitesimal quantities are *not* changes in functions of state.

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