# PROPERTIES of Matter

B. H. FLOWERS
and
E. MENDOZA

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**B. H. Flowers, F.R.S.**
*Langworthy Professor of Physics,*
*University of Manchester*

**E. Mendoza**
*Professor of Physics,*
*University College of North Wales, Bangor*

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# Editors' Preface to the Manchester Physics Series

In devising physics syllabuses for undergraduate courses, the staff of Manchester University Physics Department have experienced great difficulty in finding suitable textbooks to recommend to students; many teachers at other universities apparently share this experience. Most books contain much more material than a student has time to assimilate and are so arranged that it is only rarely possible to select sections or chapters to define a self-contained, balanced syllabus. From this situation grew the idea of the Manchester Physics Series.

The books of the Manchester Physics Series correspond to our lecture courses with about fifty per cent additional material. To achieve this we have been very selective in the choice of topics to be included. The emphasis is on the basic physics together with some instructive, stimulating and useful applications. Since the treatment of particular topics varies greatly between different universities, we have tried to organize the material so that it is possible to select courses of different length and difficulty and to emphasize different applications. For this purpose we have encouraged authors to use flow diagrams showing the logical connection of different chapters and to put some topics into starred sections or subsections. These cover more advanced and alternative material, and are not required for the understanding of later parts of each volume.

Since the books of the Manchester Physics Series were planned as an integrated course, the series gives a balanced account of those parts of physics which it treats. The level of sophistication varies: '*Properties of Matter*' is for the first year, '*Solid State Physics*' for the third. The other volumes are intermediate, allowing considerable flexibility in use. '*Electricity and Magnetism*', '*Optics*' and '*Atomic Physics*' start from first year level and progress to material suitable for second or even third year courses. '*Statistical Physics*' is suitable for second or third year. The books have been written in such a way that each volume is self-contained and can be used independently of the others.

Although the series has been written for undergraduates at an English university, it is equally suitable for American university courses beyond the Freshman year. Each author's preface gives detailed information about the prerequisite material for his volume.

In producing a series such as this, a policy decision must be made about units. After the widest possible consultations we decided, jointly with the authors and the publishers, to adopt SI units interpreted liberally, largely following the recommendation of the International Union of Pure and Applied Physics. Electric and magnetic qualities are expressed in SI units. (Other systems are explained in the volume on electricity and magnetism.) We did not outlaw physical units such as the electron-volt. Nor were we pedantic about factors of 10 (is 0.012 kg preferable to 12 g?), about abbreviations (while s or sec may not be equally acceptable to a computer, they should be to a scientist), and about similarly trivial matters.

Preliminary editions of these books have been tried out at Manchester University (and in the case of '*Properties of Matter*' also at Bangor University) and circulated widely to teachers at other universities, so that much feedback has been provided. We are extremely grateful to the many students and colleagues, at Manchester and elsewhere, who through criticisms, suggestions and stimulating discussions helped to improve the presentation and approach of the final version of these books. 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 frequently accepting, our many suggestions and requests. We would also like to thank the publishers, John Wiley and Sons, who have been most helpful in every way, including the financing of the preliminary editions.

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

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

# Properties of Matter

# The Manchester Physics Series

*General Editors*

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

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

*This series is planned to include the following volumes:*

**Properties of Matter:** B. H. Flowers and E. Mendoza

**Electromagnetism:** I. S. Grant and W. R. Phillips

**Atomic Physics:** J. C. Willmott

**Optics:** F. G. Smith and J. H. Thomson

**Statistical Physics:** F. Mandl

**Solid State Physics:** H. E. Hall

# Preface

A radical revision of the undergraduate physics syllabus of the University of Manchester was undertaken in the year 1959. This exercise involved the participation of many members of the academic staff. It was eventually decided to base the whole of the syllabus upon two introductory first-year courses, one concentrating on the general properties of wave motions, the other based upon the statistical properties of matter considered as a collection of interacting atoms and molecules. The latter course, consisting of about 34 50-minute lectures, was first given in the 1959/60 academic session under the title 'Properties of Matter'; over the years it has developed into the present book.

Our aim has been to show how the macroscopic quantities describing matter in bulk can be related to each other in terms of the microscopic properties of molecules and their interactions. This of course is the subject matter of statistical thermodynamics. To the purist this subject can only be tackled after a thorough grounding in advanced mechanics, thermodynamics and the quantum theory. But the spirit of inquiry amongst undergraduates, and the incentive to devote their time and energies to these rigorous pursuits can more readily be generated, it seemed to us, if they can first be made aware of what much of physics is about in a more rough and ready fashion. It is perhaps contrary to the present fashion, but we have omitted all quantum considerations from the foundations of this work, confining ourselves to a few passages here and there which are in the nature of 'see the next exciting instalment' when, indeed, quantum theory is necessary rather than merely desirable in order to understand some macroscopic phenomenon. Similarly, we have excluded any discussion of the second law of thermodynamics and its consequences—at the risk, here and there, of doing violence to the distinction between internal energy (which we calculate) and free energy (which we do not). We hope that we have at least identified the points at which the distinction matters. However, we consequently have not always been able to avoid the phrase 'It can be shown that . . .', although we have tried to avoid any implication of it except in peripheral matters. We comfort ourselves by suggesting that physics would be very dull unless there were always some things left outstanding in this way.

More importantly, however, we have been forced to restrict severely the number of kinds of matter we were prepared to discuss. We have excluded all discussion of ionized plasmas, of polymers and of biological materials. Each of these, it seemed to us, requires a book to itself. We have touched, although briefly, on the engineering properties of materials limiting ourselves to a discussion of the strength of real solids—for our concern has been rather to show that these properties can in principle be related to the microscopic properties. Argon, gaseous, liquid and solid, figures ubiquitously. It is perhaps the simplest element from our point of view, the ideal element, about which much experimental information is available to us for our simple-minded analysis. Apart from that, we have mostly confined ourselves to gases, liquids and solids consisting of small molecules, and to simple ionic substances and metals.

This is the way in which much of the study of the properties of matter developed historically. We hope that we have succeeded in bringing back some of the excitement of the original discoveries; certainly we found it exciting to rediscover some of these ourselves.

The course has been given in modified form in Manchester since 1959 and in Bangor since 1965, by others as well as by ourselves. We are indebted to several of our colleagues who, as lecturers or tutors, have contributed much to its gradual development. We are particularly indebted to Dr David Caroline, as well as to the editors of the Manchester Physics Series for their friendly but penetrating criticisms and suggestions. Most of all we are indebted to more than a thousand of our students whose own efforts to understand what we were trying to do has been our main encouragement and incentive. They are not, of course, responsible for the remaining imperfections in our book.

B. H. Flowers
Eric Mendoza

# List of Symbols

| | |
|---|---|
| $A, B$ | constants |
| $A$ | area |
| $A_0$ | activation energy |
| $a, a_0$ | atomic or molecular diameter |
| $\mathfrak{a}, \mathfrak{b}$ | constants in van der Waals' equation |
| $\alpha$ | linear expansion coefficient; Madelung constant |
| $\beta$ | volume expansion coefficient |
| $\gamma$ | ratio of specific heats; surface tension |
| $\gamma_G$ | Grüneisen constant |
| $C$ | specific heat, usually with suffix: $C_p$, $C_v$ |
| $c$ | speed of molecule; speed of light |
| $D$ | diffusion coefficient |
| $d$ | distance |
| $E$ | energy |
| $e$ | charge on electron |
| $\varepsilon$ | depth of interatomic potential well |
| $F$ | force |
| $f(\ )$ | function |
| $\mathscr{F}$ | faraday |
| $\eta$ | viscosity coefficient |
| $J$ | flux of particles |
| $K$ | bulk modulus |
| °K | degrees absolute |
| $k$ | Boltzmann's constant |
| $\mathrm{K}$ | velocity coefficient of chemical reaction |
| $\kappa$ | thermal conductivity |
| $\mathscr{K}$ | kinetic energy |
| $L_0$ | latent heat at low temperatures |
| $\mathscr{L}$ | Lorentz number |
| $\ell$ | length |
| $\Lambda$ | wavelength |
| $\lambda$ | mean free path |
| $M$ | molecular weight |
| $m$ | mass of atom |

| | |
|---|---|
| $N$ | Avogadro's number |
| $n$ | number, number density |
| $\mathfrak{n}$ | coordination number |
| $\mathcal{N}$ | number per unit area |
| $\nu$ | frequency |
| $\nu_{\mathrm{E}}$ | Einstein frequency |
| $P$ | pressure |
| $P[\ ]$ | probability function |
| $p_x, p_y, p_z$ | momentum components |
| $p, q$ | indices of interatomic potential energy |
| $r$ | radial distance |
| $\rho$ | density |
| $s$ | strain |
| $\sigma$ | collision cross-section; conductivity |
| $T$ | temperature |
| $t$ | time |
| $\tau$ | characteristic time |
| $U_x$ | drift velocity |
| $V$ | large volume |
| $V_0$ | molar volume |
| $v$ | small volume |
| $v_x, v_y, v_z$ | velocity components |
| $\mathcal{V}$ | potential energy |
| $\omega$ | angular velocity |
| ★ | sections or subsections marked with a star may be omitted, if the reader so wishes, as they are not required later in the book |

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## 4 ENERGY, TEMPERATURE AND THE BOLTZMANN DISTRIBUTION



## 5 THE MAXWELL SPEED DISTRIBUTION AND THE EQUIPARTITION OF ENERGY



## 6 TRANSPORT PROPERTIES OF GASES



## 7 LIQUIDS AND IMPERFECT GASES



★Starred sections or subsections may be omitted, if the reader so wishes, as they are not required later in the book.

CHAPTER 1

# The study of the properties of matter

## 1.1 THE STUDY OF THE PROPERTIES OF MATTER

Throughout the whole of the nineteenth century, one of the open questions of science was whether matter was composed of atoms or not. Nobody had yet been able to perform experiments with single atoms, certainly no-one had ever seen one, and for a long time no-one knew even the order of magnitude of the sizes of atoms—whether their diameters were typically of order $10^{-5}$ cm or $10^{-50}$ cm. One method of attack was to try and *correlate* as many different properties of solids, liquids and gases as possible on the basis of simple postulates about the forces which atoms exerted on one another. The earliest attempt at describing these forces was made by Boscovitch in 1745. Sixty years later, a triumph was scored when Laplace, arguing from the fact that the rise of a liquid in a capillary tube was observed to be independent of the thickness of the wall of the tube, deduced that atomic forces must act only over short distances. He was able to deduce theoretically the form of the surface-tension law for liquids, that the force exerted by surface tension should be proportional to the length of a cut in the surface—and this was verified experimentally. Much later, in the 1860's and 70's, the transformation of gas into liquid was demonstrated for many substances when it became technically possible to produce high pressures and low temperatures. The similarities and regularities in behaviour of several substances, predicted on the basis of crude atomic models, added plausibility to those models. Above all, the rough agreement between estimates of the *sizes* of atoms based on widely differing kinds of experiments (about eight completely different methods all gave atomic diameters of the order of $10^{-7}$–$10^{-8}$ cm) made the atomic hypothesis fairly secure by 1900.

Thus the subject called 'Properties of Matter' or 'Heat' was at one time an exciting one. Physicists measured surface tensions and latent heats and elasticities and tried to correlate them under an all-embracing atomic theory. But with the discovery of sub-atomic particles and the invention of counting devices which could detect single atoms or ions, the subject lost its urgency. By the early years of the twentieth century, no-one anywhere doubted that matter was atomic in structure and that atoms were of the order of $10^{-8}$ cm in diameter. Experimenters still measured surface tensions, latent heats and elasticities, but these had now become respectable, if routine, activities in their own right. Books came to be written entitled 'Properties of Matter' which described highly sophisticated apparatus for measuring quantities of this kind, and gave elaborate calculations on the twisting of laminas and the bending of beams, but never mentioned the word 'atom'.

It is the purpose of this book to try and recapture some of the spirit of the old approach. We will in fact *start* from statements about the shapes and sizes of atoms and the forces holding them together, and then show how the properties of solids, liquids and gases can be deduced. It is our purpose to show that, given the potential energy between two atoms of known atomic weight, it is possible to estimate the density of the solid and its specific heat, its thermal expansion and elasticity, the surface tension and latent heat and viscosity of the liquid, the diffusion constant and thermal conductivity and specific heat of the gas and the velocity of sound through it: they are all *related* properties of matter.

## 1.2 ORDERS OF MAGNITUDE

The estimates we shall make will rarely be exact ones. Since the object of our discussions will be mainly to show that we can identify the forces or mechanisms underlying certain phenomena, it will serve our purpose if we can show that using approximate methods we can get *roughly* the right answer. To improve on rough estimates usually demands a great increase in mathematical complexity, and it would achieve little if we risked obscuring the line of the argument by getting involved in complicated manipulations merely to add a few percent to the accuracy of the result. In many operations, it is by contrast extremely important to know

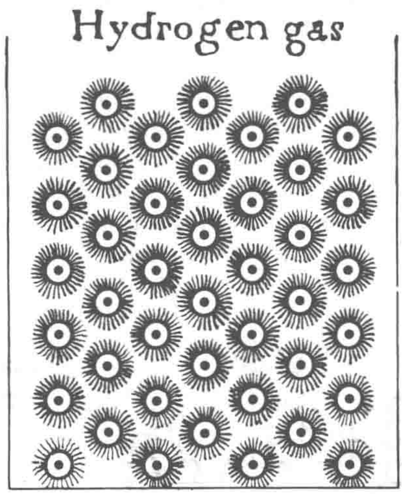


Fig. 1.1. A diagram drawn by John Dalton, in his epoch-making book *A New System of Chemical Philosophy* published in 1810. The gas is shown as a *regular* arrangement of atoms, which is quite wrong. Not till this idea was supplanted could any real progress be made.

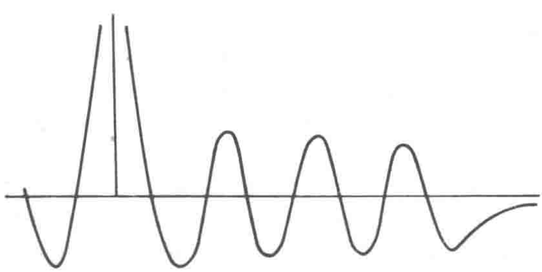

Fig. 1.2. An early idea of the effect of one atom on another—from a book published by Boscovitch in 1745. Compare this diagram with Fig. 3.4. The oscillations in this graph were postulated to account for the structure of a gas as pictured above, but this remains an astonishingly penetrating attempt to explain the properties of matter in fundamental terms.