MICHAEL de PODESTA

UNDERSTANDING THE PROPERTIES OF MATTER

SECOND EDITION

Understanding the Properties of Matter

Second Edition

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Understanding the Properties of Matter

Second Edition

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For...

Maxwell and Christian
John and Maíre
You and me

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Foreword to first edition

Professor Sir Brian Pippard, FRS

One of the greatest transformations of physics began about 70 years ago, when quantum mechanics was formulated. Many of the outstanding puzzles of atomic structure suddenly became clear, and it was not long before a start was made on understanding the chemical bond. Before 1930 the new ideas were applied to solids; one of the first successes was to explain how electrons can move so easily between the closely-packed atoms of a metal, and soon after this came the explanation of why some solids conduct electricity well, but others are insulators. Since then there has been no slackening of effort; many more phenomena have been revealed and explained, and new technologies have grown up out of the successes, to transform our lives. One example will suffice. The transistor was invented in 1947 by solid-state physicists, and without it modern communication and information systems would never have been developed.

There are more people engaged in research into condensed matter, and its applications, than on any other branch of physics. One consequence of this activity is that the assimilation of new facts and theories is an almost overwhelming task, and we are forced to rely on the efforts of those who can put together a readable account of the main themes. It is not surprising that most of the recent text books meet the challenge by concentrating on general principles and the theoretical treatment of rather simple examples, to such a degree that a casual reader might consider that the whole subject is dominated by theory. One cannot deny that without theory we should be left with a miscellaneous ragbag of facts, lacking the means to find any underlying structure. On the other hand, without the challenge of the facts, the deep general theories like quantum mechanics would never have been looked for.

Nowadays most physicists specialise in either experiment or theory, and there are few to rival those of earlier days who, like Maxwell, Rayleigh, Helmholtz and Fermi, were superlatively good at both. Nevertheless, all modern specialists acknowledge their dependence on the different skills of others. A theoretician ignorant of facts is no more to be trusted than an engineer who takes a textbook diagram of a bridge as the basis for a design, never having seen the real thing or tested a model. Unfortunately the prevalence of software packages for almost every conceivable task encourages the mistaken belief that they incorporate all the experience needed for success in their application. If you read Michael de Podesta's book seriously you are unlikely to fall into such a grievous error. Once its lesson has been learnt, it will remain a source of information and, more important still, an incentive to continue with the process of self-education, which is the key to achievement.

Of all the messages that this book conveys there is especially one with which I feel the strongest sympathy. It is not that facts are things you have to assimilate before you settle down to interesting theories – rather, it is that the facts themselves, if well presented, are interesting in their own right and raise a host of questions that make you want to find out how everything ties together. All too rarely do most of us stop to think about apparently trivial everyday observations. How often, for example, do we wonder why there are such things as liquids? You will not find a complete answer here because the complete answer is not known (and perhaps least understood about water, that most extraordinary of liquids) but you will discover the beginning of an answer, and you will find that the beautiful simplicities of thermodynamics help you to see what happens when a solid melts, and give hints of the difficulties that one may yet hope to eventually overcome. And this is only one of the tantalising problems discussed here in the hope that you will discover (if you have not done so already) both the lovely certainties and the stimulating mysteries that together make physicists enjoy their work, and continue to enjoy it as long as they can carry on with physics.

Acknowledgements

Despite the fact that only one name appears on the cover, and despite the essentially solitary nature of writing, no book of this kind can ever truly be written by a single person. Every author is indebted in all kinds of ways, to all kinds of people, and I am no exception. What follows is a list of the major debts I have incurred while writing this book. I would like to thank my benefactors and ask simply for some time to be able to repay them.

My first, and largest, debt is to Stephanie Bell, my wife, and to Maxwell and Christian, my children. They have tolerated, supported and encouraged me, through months of late nights and working weekends.

My second debt is to the many academic colleagues with whom I have worked over the years. From the Physics Department at Birkbeck College; the Condensed Matter group at University College London; and at the Open University.

My third debt is to those who were kind enough to comment on the First Edition, particularly Bertil Dynefors, Gabe Spalding and Paulo Manuel de Araújo Sá, who produced detailed (and embarrassingly long) lists of errata. Every one of *these* mistakes has been eliminated!

My fourth debt is to the staff at *Taylor and Francis*. In particular, Grant Soanes for allowing me the opportunity to work on this revised edition, and Peter Willis for his help, kind words, and attention to detail.

I now work for the UK's National Physical Laboratory and I would like to thank my many colleagues there who have (often unknowingly) contributed to this book. I would also like to thank David Robinson for permission to take a months leave during which I was able to complete my first revision of the text.

And, as with the first edition, I would like to acknowledge the work of those scientists, living and dead, who have faithfully recorded their observations of the physical world. Without their care and attention to detail, it would not have been possible to write this book.

Finally, if you have any comments, good or bad, I would be happy to receive them. Any helpful comments on the text will be posted on the web site for the book (www.physicsofmatter.com).

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Constants

The fundamental physical constants are known to much greater precision than is shown in this table, but the precision shown is sufficient for all the work in this text, and almost all work related to the physics of matter. For more precise values and uncertainty estimates the reader should consult *Tables of physical and chemical constants* by *Kaye and Laby*, referred to in §1.4.1

Constant and symbol	Value	Unit
Speed of light in vacuum, c	2.998×10^{8}	m s^{-1}
Electric charge on proton, e	1.602×10^{-19}	C
Planck constant, h	6.626×10^{-34}	J s
Planck constant, $(h/2\pi)$	1.054×10^{-34}	J s
Mass of proton, m_p	1.673×10^{-27}	kg
Mass of electron, m_e	9.109×10^{-31}	kg
Atomic mass unit, u	1.661×10^{-27}	kg
Electron volt, eV	1.602×10^{-19}	J
Bohr magneton, μ_B	9.274×10^{-24}	J T^{-1}
Boltzmann constant, k_B	1.381×10^{-23}	J K^{-1}
Avogadro number, N_A	6.022×10^{23}	mol^{-1}
Molar gas constant, R	8.314	J K^{-1} mol^{-1}
Permeability of free space, μ_o	$4\pi \times 10^{-7}$	H m^{-1}
Permittivity of free space, ε_o	8.854×10^{-12}	F m^{-1}
Stephan–Boltzmann constant, σ	5.671×10^{-8}	W m^{-2} K^{-4}

CHAPTER 1

The quest for an understanding of matter

1.1 Welcome

People have wondered about the properties of matter for many centuries and have written many excellent books on the subject. Even books that were printed half a century ago are relevant today. The properties of matter, and our theories about matter, have changed relatively little in this time. This is not to say that new phenomena have not been discovered and explained: for example superfluidity and superconductivity have been exciting areas of advance in understanding. However, the laws of thermodynamics have not changed and the speed of sound in copper is the same as it was 100 years ago. The scientists who have worked during this century have left you, students of physics in the new century, a truly vast legacy of experimental results and theoretical analysis. Your mission, should you choose to accept it, is to acquaint yourselves with this legacy.

The study of the properties of matter is like an ancient party. Over millennia, it has at times been quiet, at times riotous. Famous figures have attended, but most of the people here are just like you and me. As I write today, the party is bustling after a century or so of explosive chitter chatter. What will happen next? I have no idea, but I expect it will be interesting. I hope you will stay to find out.

1.2 Personal experience

More than half a lifetime ago I was a student of physics. From the manner in which I was I taught the various elements that comprise the study of matter, I learned several lessons that it has taken me a long time to unlearn. Firstly, I learned that it was not necessary to actually know what the properties of matter were in order to debate them earnestly. This is, of course, rubbish. However, fear of my own ignorance prevented me from realising this earlier. Secondly, I learned to avoid thinking about awkward subjects. I imagined that cleverer people than myself had sorted these things out. This is rubbish too, but fear of my own ignorance still haunts me here.

In hoping that your experience will differ from my own, I would urge you develop your study of the properties of matter along the following lines. Firstly, 'make friends' with matter: become familiar with what the properties of matter actually are. These properties have been determined and tabulated for thousands of substances so it is not difficult. I believe that unless you are familiar with the properties of matter it is impossible ever to say that you understand them. Secondly, and also secondarily, try to think about why things are the way they are. Often the data seem perplexing, but they usually make sense eventually.

1.3 A historical perspective

1.3.1 Discovery and rediscovery

Before embarking on this contemporary study of the properties of matter, it is instructive to spend some time reviewing the historical context in which this study takes place.

In all aspects of my own work as a scientist, I am constantly reminded that 'others have been here before'. That although I am discovering particular facts for the first time, these facts are leading me to re-discover the insights of previous generations of scientists. These scientists lacked the technical resources available today, but in their place used resourcefulness, dedication and imagination in a truly inspiring combination.

After overcoming my depression at the dimly retreating prospect of scientific stardom, I have realised that this process of rediscovery is not failure. Indeed it was – and is – the essential process through which the health of the scientific body is maintained. Further, I realise the process is not the work of a degree course, but of a lifetime. If you wish to learn about physics, the only way is to rediscover it for itself.

Unfortunately, rediscovery is as hard as discovery, but without the glory. In writing this book I have tried to ease your work of rediscovery of the properties of matter. I have written this book by collating data on the properties of matter, writing down a list of questions that occurred to me as I examined the data, and then trying to answer these questions on your behalf.

1.3.2 Familiarity and over-familiarity

The initial section of each topic in this book is a discussion of the data on that topic. Before discussing the theories about what happens, I wish you to become familiar with what actually happens. In this way I hope to allow you to rediscover some of the more striking properties of matter for yourself.

However in encouraging this familiarisation I encounter a severe problem. The problem of an improper over-familiarity with rather sophisticated theories about matter. For example, many of you reading this will have seen images of atoms: you will have heard or even taken part in discussions of their detailed structure. I would go so far as to say that many of you believe in atoms. However I would also venture that many of you believe in atoms not because of insights you have made yourself, but because you have been told that they exist and you have been told that they possess certain properties. I am sure your teachers have taught you well, but being told something is different from convincing yourself it must be so. This is the sense in which I would like you to embark upon the study of matter. Do not believe it until you have seen the data! I would like you to be sceptical about the data in this book, about the theories presented here, and most of all about your own credulity.

1.3.3 Consciousness lowering

In order to help get in the mood to rediscover the properties of matter, you may care to take part in an exercise in 'consciousness lowering'.

Picture yourself in the late seventeenth century, look around you. The 'stuff' of the world – the matter – is diverse in its properties. You can probably see wood, metal, stone, paper and – most amazingly – animated flesh. Your task is to categorise these substances and their experimental properties. What do they have in common? How do they differ?

In other words, you must decide on a set of organisational principles which will allow you to found an understanding of matter. Notice that you cannot include references to concepts which we now accept such as atoms, or electric charge. These are concepts which you must develop by studying matter – categorising results, preparing hypotheses, worrying about exceptions – and trying to convince a sceptical group of colleagues that your insights are valid. I think you will find it extraordinarily difficult to know where to begin, and if you wish to see the task through, I should set aside a lifetime or so for the purpose. The bewildering variety of the properties of matter will provide exceptional cases for just about any scheme of categorisation you adopt.

And if you find this process of categorisation difficult, pity then people from earlier times who reflected on the nature of matter. They suffered both from a lack of reliable data, a lack of validated concepts for understanding the data, and the experimental equipment of the same type as a 13-year old might use in a modern teaching laboratory. I wonder how long it would have taken you to 'discover' atoms and determine their properties; to 'discover' that there are two types of electric charge; to 'discover' that heat is not a substantive fluid.

All your present clarity of vision, such as your wise belief in the existence of atoms, has been constructed on a foundation of centuries of sceptical enquiry.

1.3.4 Organisational principles

What the above exercise is intended to show is that it is not obvious what organisational principles we should use in attempting to categorise matter. And without the appropriate organisational principles, the properties of matter are bewilderingly diverse and explanations appear arbitrary and unconvincing. So, how should we choose to categorise matter?

Animate/inanimate

The first categorisation that suggests itself to me is that between animate and inanimate matter. Historically, division of the study of matter in this way allowed the emerging science of physics to appear successful at explaining and parameterising the simpler properties of inanimate matter. By contrast, the study of animate matter is still barely beyond the stage of naming and categorising.

Solids, liquids and gases

Considering the inanimate world, the next most apparent organisational scheme is the classification of matter into one of three categories: solid, liquid or gas. This rather natural categorisation is now seen as by no means exhaustive. (Indeed it never was: our own bodies are made from matter which is half-liquid and half-solid.) Liquid crystals for example disclose by their very name that the solid-liquid-gas categorisation is inadequate. Further, substances normally considered to be in one category (such as 'solid' rock) when viewed over geological time scales shows properties associated with the liquid state (such as flow and convection). However the solid–liquid–gas division is still a useful one, and forms the basis for the structure of this book.

The conceptual division of matter into distinct categories of solid, liquid and gas was historically extremely important. Once made, real progress became possible in understanding the properties of the simplest of the category of matter: the gaseous state. In studies of gases over the two hundred years from 1700 to 1900 an enormous number of ideas emerged and were tested. In particular the nature of four key concepts were distilled into a form somewhat similar to the one we hold today. The key concepts were descriptions of the properties of matter in terms of atoms, the nature of heat, electricity, and light As we examine the properties of gases in Chapter 5, bear in mind that with the exception of our reference to quantum mechanics, the study would not have been out of place a century ago!

1.4 The structure of this book

The structure of this book is shown in Figure 1.1. Chapters 1 to 3 provide respectively, the context of the book, a mini revision course on some relevant background theory, and a discussion of some aspects of the process of measurement. Chapters 4 to 11 comprise the main text of the book. Gases are discussed in Chapters 4 and 5, solids in Chapters 6 and 7, liquids in Chapters 8 and 9. The transitions between these states of matter are considered in Chapters 10 and 11. The first of each pair of chapters outlines relevant background theory, while the second considers the experimental data, and the extent to which they can be understood using the background theory. Where relevant, the theory is extended to understand the data.

Chapter 12 contains a set of 30 questions which are considerably more involved than the end of chapter exercises. They are arranged under the headings of gases, liquids, solids and phase changes.

The appendices contain detailed points of theory which are important, but which would tend to distract attention from the flow of the text if placed within the chapters.

At www.physicsofmatter.com

In any book there is a conflict between the desire to include more material, and the desire to prevent the book becoming unreadably large. In this second edition, I have attempted to improve on the compromise I chose for the first edition by placing additional material on the internet. This has allowed me to present additional material on several important topics that were briefly covered in the first edition, while simultaneously keeping the core text at the same size. All the extension topics are available for free download from the web site:

`http://www.physicsofmatter.com/`

At this site, you will find copies of all the figures and tables used in the text. You will also find copies of several of the data tables in a format which may be used with the spreadsheet programs available on most personal computers.

Figure 1.1 The structure of this book.

In the text:

2	**Background theory**	
3	**Measurement**	
4	**Gases**	Background theory
5		Comparison with experiment
6	**Solids**	Background theory
7		Comparison with experiment
8	**Liquids**	Background theory
9		Comparison with experiment
10	**Changes of Phase**	Background theory
11		Comparison with experiment
12	**Questions**	
	Appendices	

At www.physicsofmatter.com:

W1	**Band theory of solids**
W2	**Magnetic properties of solids**

1.4.1 Data sources and bibliography

The data in this book has been compiled from a variety of sources. All the sources are secondary: that is they have already been compiled by somebody else from primary data in research literature. These secondary sources are enormously useful in all areas of physics and I would urge anyone contemplating a career in physics to buy them and treasure them. The main sources of data used in the compilation of this book are:

- G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants*: 14th, 15th and 16th Editions, published by Longman (Harlow) in the UK and Wiley (New York) in the USA. This is referred to as *Kaye & Laby* in the text.
- Weast *CRC Handbook of Chemistry and Physics:* 65th *Edition* [also known as the 'Rubber Bible'], published by Chemical Rubber Publishing Company (Chicago, Ill)
- John Emsley, *The Elements*, published by Clarendon Press / Oxford University Press (Oxford).

References to electromagnetic theory are to the excellent

- B.I. Bleaney and B. Bleaney, *Electricity and Magnetism* [two volumes] published by Oxford University Press (Oxford).

Other sources are given in the text. Where no reference is given in the text, the data have been compiled and cross-checked from several sources. I have tried, by several techniques, to eliminate erroneous data from my compilations. However, I cannot guarantee this, and you are referred to the original compilations and the references therein. The web site for the book also contains an up-to-date list of errata.

1.5 Exercise

Exercises marked with a P prefix are 'normal' exercises. Those marked with a C prefix are best solved numerically by using a computer program or spreadsheet. Exercises marked with an E prefix are in general rather more challenging that the P and C exercises. Answers to all the exercises can be found on the web at www.physicsofmatter.com

P1. Isaac Newton was (obviously!) unaware of developments in electromagnetism, quantum mechanics, genetics and evolutionary theory. However, in my opinion, his view of the world was undoubtedly 'modern'. Obtain a copy of Newton's work *Opticks* (New York: Dover) and read the final section marked 'Queries' (page 339 in the Dover edition). This consists of a number of questions over which Newton had puzzled, and to which he had arrived at tentative answers. After reading his 'Queries', carry out the following exercise.

Imagine that Newton were to return to life in our time, and it fell to you to explain to him the key developments in modern science since his death. Write the script of a half-hour conversation between the two of you. Remember, you haven't got long so (a) don't waste time telling him about what he already knows and (b) be sure to script Newton's part as well as your own. I imagine he would be rather ill-tempered and aggressive, but compulsively curious. So he would be sure to interrupt if he didn't understand the language you were using and would be sure to say things like 'Yes, yes, I suspected that all along'.