The theory of thermodynamics

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(Sections marked with an asterisk may be omitted at first reading.)

Preface

This is a textbook on the theory of heat for university students, primarily for students of physics and chemistry. The plan of the book is explained at the end of Chapter 1: this preface is more particularly concerned with the aims which the author hopes to achieve. In assessing existing texts and in organising the material I have had three points in mind. First, the *logic* of the theory of heat is notoriously obscure to students. In dealing with this branch of physics, they often feel themselves out of touch with the underlying principles, and, when faced with a calculation, are unsure of what approach to adopt. My first aim, then, has been to present the principles of the subject as coherently and concretely as possible. Second, it seems surprising that there is no single text on heat which a first-year student can buy and use in the knowledge that it will carry him through to his final year and beyond. This book is designed as an exposition of the theory of heat whose early parts may be understood by an able school leaver, but which is nevertheless a solid final-year text. Third, I am irritated, in texts at all levels, by much obscurity and exaggerated awe concerning the statistical principles upon which the theory of heat is based. I have therefore made an effort to present the starting assumptions of the subject clearly and in quite simple terms from the outset. This is not to deny that, as in other areas of physics, the fundamental notions turn out when rigorously examined to be of considerable difficulty and subtlety. Some of the difficulties and subtleties *are* explored in this book, but not until late in the treatment.

With these aims in view, it was important to work for a clear and compact presentation with relatively little illustrative material, so that my reader should quickly come to see what depends upon what. The chapters are laid out to display the logical structure of the subject which I hope that he or she will have accepted by the end of the course. The fundamental principles come first, and deductions follow. Moreover, the book is cross referenced using a system of marginal notes which makes it easy to locate particular topics, to trace arguments backwards and to anticipate later developments.

In using such a book, two points should be noted. Firstly, it is a book about *theory* – the sort of theory that experimenters should know and enjoy.

This means that it must be supplemented by illustrative material, which is provided in the text itself by a range of problems at the ends of the chapters: the student who tackles these problems energetically will not be short of illustrations of the ideas in action, but, unless he is quite unusually bright, he will need help and guidance in answering some of them. Secondly, although the book starts easily, in overall scope it is a final-year text. To make it more useful for elementary or specialised courses, I have arranged that certain subsets of ideas may be pursued in isolation. These subsets are identified under boldface headings in the index. In particular, there are two self-contained elementary courses, one on *classical thermodynamics*, which makes no use of the microscopic pictures of temperature and entropy, and one on *temperature, Boltzmann factors and elementary kinetic theory*, which does not involve the concept of entropy. There is also an abbreviated course on *chemical thermodynamics*. From Chapter 12 onwards the writing is aimed at students near the ends of their undergraduate careers, and a basic background in classical and quantum mechanics is assumed. In these later stages, and especially in the final chapter, I have not hesitated to expose the reader to advanced ideas, not normally regarded as undergraduate material, but without going into detail. At all stages of the book, sections marked with an asterisk may with advantage be omitted on first reading.

Argument concerning the true justification of statistical thermodynamics never ceases, and I shall not, I am sure, escape criticism from the experts for basing this book on Fermi's master equation. I have chosen to do so not because I believe the master equation to be the ideal logically fundamental starting point – as Chapter 19 shows, it is certainly not that – but because, from experience of teaching the subject, I find it the *only* starting point which is understandable at the beginning of the course, is not shrouded in mystery and does no violence to the essential physics. Moreover, it exhibits at the outset the intimate connection between kinetics and thermodynamics, giving the student confidence that he understands the nature of the argument, and it has for him a practical and familiar air, being directly related to the sorts of kinetic calculation which he is likely to have met in scattering or reaction theory. In the same spirit I have introduced statistical temperature (following recent practice in other books) by considering the physical properties of large heat baths rather than the mathematical properties of large ensembles, and defined statistical entropy from the outset as a measure of the logarithm of the number of quantum states over which the probability is spread, primarily because I know that students find definitions which are linked to an explicit physical picture the easiest to grasp.

It is a pleasure to thank Rex Godby, David Newson, Nick Safford, Charles Taylor and Chris Williams of Pembroke College, who took time from exam revision or research to read and comment on the various drafts, and my colleagues in the Cavendish Laboratory, Brian Pippard and Gil Lonzarich, who have reviewed the complete typescript, and, since they both know more

about this subject than I do, have been well able to keep me on the rails. As is usual, they are not to be counted responsible for the outcome; and yet Professor Pippard must bear some sort of indirect responsibility, for he has been expounding physics to me for half my life, to my great pleasure, and I hope that he will continue in this task. Susan Cole and Jan Thulborn prepared the typescript, while at the University Press Simon Mitton, Sheila Shepherd and Jack Bowles guided the planning and organised the text for the printers.

A number of the problems at the ends of chapters are modified versions of Cambridge Tripos Examination questions or exercises which appeared originally in *Cavendish Problems in Classical Physics*, edited by A. B. Pippard and published by Cambridge University Press. I am grateful to the University, the University Press and Professor Pippard for permission to use this material, and to the American Physical Society, Dr B. J. Alder and Dr T. E. Wainwright for permission to reproduce Fig. 14.6. Where other figures and tables have been based on published work the sources are acknowledged in the text.

The happy tradition of dedicating even technical books is worth preserving. This one is respectfully offered to the two teachers who, at different stages, first made its subject intriguing to me. I hope that, in its turn, the book will prove useful to a new generation of students.

John Waldram,
Cavendish Laboratory,
March 1984