

## PREFACE

This book serves both as a graduate text and as a reference. Statistical mechanics is a fundamental branch of science which has made substantial progress in the past decade, opening up many new areas of research. The aim of this book is not to give a complete introduction to this field, but rather to give a clear exposition of the most basic principles, and to use relatively up-to-date material as examples of application. Concepts as well as applications are thus emphasised.

The statistical mechanics of today is so fragmented into subfields and so extensively applied to various phenomena that the reader cannot hope to become an expert by just reading one or two textbooks. This text merely aims at helping the reader establish a solid foundation on the principles, clarify some concepts, as well as learn some simple 'tricks' so that he can cope with new problems himself. At the time of writing, there are already many textbooks around including many classics. But they now look somewhat old-fashioned both conceptually as well as in content. On the other hand, many new books are too specialised. Scientists are now heavily devoted to research, and they expend less effort in writing books. In addition, new knowledge accumulates rapidly, so much so that it is extremely difficult to write a textbook which can stand the test of time. This book is a short one, serving the need of students for the time being. I hope that it can be of use to contemporary readers.

Statistical mechanics is a branch of theoretical physics, distinguished by its extensive applications in physics, astronomy, chemistry, materials science as well as biology. It is a convenient tool to link the molecular structure and properties with the macroscopic thermodynamic and electromagnetic behavior. The application of statistical mechanics can be classified according to its degree

of difficulty as “elementary” and “advanced”. The elementary part is essentially the ideal gas, including the quantum ideal gas. It includes all cases when the interaction between particles is unimportant; the free electron model is one of these cases. Its application is rather extensive. The advanced part discusses the interaction, which plays an important role in many problems, for example in the phenomena of phase transitions. Naturally, the advanced part is much more difficult. Except for some special cases, approximation and numerical calculation are the only methods of solution. The simple and effective approximations usually simplify the problem to certain models of an ideal gas. The mean field approximation is an important example.

In my view, advanced statistical mechanics is a product of the emergence of solid state physics. Although the relation between statistical mechanics and phase transitions is forty years old, most of the applications and developments were made within the last twenty years. The field especially has been fertile in the last ten years. Most of the applications are on solid state, because the phenomena in solid state are numerous, the experimental techniques have become increasingly sophisticated and the physical systems to be investigated are not as complicated as biological systems. Hence the theoretical analysis can cope with such systems. Many new concepts, in fact, originate from solid state physics.

The greater part of this book is on the discussion of examples. The elementary examples are used to clarify the concepts, while the advanced examples are used to discuss the phenomena and methods. In fact, the basic principles and the applications are inseparable. All the examples in this book are used, directly or indirectly, to illustrate some basic concepts. The examples are selected for their extreme simplicity. The material is somewhat biased towards phenomena in solid state physics and I have tried to include some modern, interesting and inspiring topics, in the hope of providing the reader with a glimpse of the modern developments in statistical mechanics.

One motivation for writing this book is to air some of my personal views. My views on some of the basic concepts differ from the conventional ones. I think that statistical mechanics, as it is at present, is an ill-proportioned subject, with many successful applications but relatively little understanding of the basic principles. Yet most textbooks treat statistical mechanics as a complete science.

Roughly speaking, statistical mechanics is based on some rules of calculation. We can proceed forward and discuss the application of the rules of calculation, or we can turn back to discuss their origin. (These rules or calculation can be said to be the Boltzmann’s formula for the entropy, which is equivalent to the

statement that a state occurs with a probability proportional to  $e^{-H/T}$ ,  $H$  being the energy of the state and  $T$  the temperature). There are many examples of applications, but works on the quest for the origin are relatively rare, especially at the textbook level. One reason is that, over the years, the applications have been so successful that a substantial degree of confidence is now attached to these rules of calculation. Although the origin may not be clear, the problem seems almost irrelevant because the rules are so useful and successful.

There is another reason. At present we still do not know how to start from mechanics and proceed to understand these rules of calculation; these rules are still an assumption. Many books start from the rules of calculation, ignoring their origin, and treat statistical mechanics purely as a matter of mathematical technique. This viewpoint has its validity. However, some textbooks attempt to make up for the lack of a firm conceptual foundation by giving fancy arguments to set up these rules as established laws. If students do not understand these fancy arguments, it does not matter, so long as they can still use the rules to calculate. This was my own experience as a student.

Of course, many successful applications do not require a profound and exact understanding. This is characteristic of scientific development. Nevertheless, if the range of applications is extended, problems will sooner or later appear. A deeper understanding will become urgent. Today the development of statistical mechanics has reached the point of delving into its origin.

The basic assumption in statistical mechanics is in fact an assumption of independence or randomness. If we can understand this assumption, then it would be helpful in understanding other stochastic phenomena, such as random number generation in the computer. The converse is also true.

We think that the proper attitude to science and to knowledge in general is expressed by the Chinese saying, "Recognise what you know, and recognise what you do not know." Hence this book pays much attention to all the weak points in statistical mechanics, the limitations on its rules of calculation, as well as its questionable and ambiguous points. Although this book does not provide the answer to the important questions, I have at least tried to state the questions clearly.

From the experience of learning mechanics and electromagnetism, the students are accustomed to precisely stated laws. Yet I constantly remind the reader of all those questionable points in statistical mechanics. It may engender a feeling of unease. I hope that this feeling of unease will make the reader become more cautious, cultivating the habit of not accepting too much on faith.

This book is divided into seven parts totalling thirty chapters. These seven

parts are

Part I	Equilibrium	Chapters 1 to 4
Part II	Hypothesis	Chapters 5 to 9
Part III	Probability	Chapters 10 to 13
Part IV	Applications	Chapters 14 to 19
Part V	Dynamics	Chapters 20 to 22
Part VI	Theoretical basis	Chapters 23 to 26
Part VII	Condensation	Chapters 27 to 30

Part I is a warm-up. It reviews some common concepts and terms, as well the theory of the ideal gas (including the quantum ideal gas).

Part II, III and VI emphasise the basic concepts. Statistical mechanics is established on a daring assumption. The meaning of this assumption is by no means clear. This book discusses this assumption from the point of view of the underlying molecular motion, avoiding abstract concepts such as “ensembles”. My view is that the concept of ensembles is unnecessary and indeed not compatible with reality. Probability is regarded here as a way of handling statistical data. It is a tool, not a theory.

Part V discusses some non-equilibrium phenomena, with a view to elucidate the maintenance of equilibrium. Metastable states and numerical simulation are included in this part.

Part IV and VII analyse various phenomena, as applications of the theory. Included are some discussions on frozen impurities, superfluidity and the two dimensional Coulomb gas. The contents are not a report of the results in the literature, but are my own understanding of these problems expressed for the reader in the most direct fashion I know. My view on these problems may not be the most appropriate and the treatment given here reflect my personal prejudices. The reader must read these chapters with this in mind.

The discussion in this book are not too rigorous; that is to say, many conclusions are not rigorously proved, but only illustrated by simple examples. I do not mean to say that rigorous proof is not important, but it is beyond the scope of my expertise. The mathematical prerequisite for this book is not high, and the necessary calculational techniques are few. There are in fact no complicated calculations in the book at all. Complicated calculations are no doubt very important, but I think that the necessary techniques can be acquired only through actual practice, and it is of no great use to include a lot of complicated calculations here in the book.

Some very important but specialised topics have not been covered in this book.

These include critical phenomena and the renormalisation group (although the phenomena of phase transitions occupy many pages in this book). Non-equilibrium phenomena are little talked about. Examples are biased to problems in solid state. There is also little on thermodynamics and in general, abstract formal things are avoided. Some materials in the book appeared in journals but not in current books; for example the relation between the virial coefficient and the collision time in Chapter 14, the echo phenomena in Chapter 24 and the calculation of entropy from the trajectory in Chapter 25. Many points of emphasis and approach differ from that of standard textbooks. For example, we emphasise the relation of the observation time with equilibrium, the importance of the metastable state and the intimate relation of superfluidity with the conservation of the winding number.

No profound mathematical prerequisite is necessary for reading this book. The mathematics used in undergraduate quantum mechanics is sufficient. The reader should be acquainted with mechanics, quantum mechanics, thermodynamics and electromagnetism. Rather, this book requires the reader to have a cautious and independent mind. Statistical mechanics is a difficult subject in basic physics and this book is not easy to study. Problems are an integral part of the contents. If the reader does not do the problems, he cannot learn the techniques of application, and he may even miss the basic concepts.

The reader should remember that the contents of this book as well as those of other books are not what you understand. Your own understanding of statistical mechanics is acquired through your own thinking and work. This book as well as others are for your reference. You should not be led along blindly.

I have another motive in writing this book. Scientific texts in Chinese are extremely scarce today, and I hope this book may be of some help in alleviating this situation. I deeply feel that basic sciences should be taught in one's own tongue, and textbooks should be written by scientists who are native speakers of their languages. In this century, scientists have become accustomed to writing research reports in the languages of the West. If asked to write a book in Chinese, the answer would often be that one is unable to do so, whereas the truth is that one does not try. The standard of my Chinese is humble, and writing this book was a bold attempt. In the beginning, I found the writing difficult, but I gained fluency as I went along. Indeed science is not literature, and there should be no problem in writing scientific books in one's own language, provided the contents are there. If this book is not easy to read, it is mainly due to the complexity of the content. That the presentation in Chinese is short of fluency is but a secondary factor.

Most parts of this book were written during my stay at the National Tsing Hua University in 1977 and 1981. Many professors and the students have offered me advice, help and encouragement, especially Professors Y Y Lee (李怡嚴), Y Shen (單越), E Yen (閻愛德), W T Ni (倪維斗), Y M Shih (石育民), H M Huang (黃幸美), T L Lin (郎棣), H C Yen (顏晃微), T T Chen (陳通) and graduate students C L Lin (林其隆), F K Yang (楊芳鏗), J L Chen (陳俊良), and D G Lin (林達觀). I express my gratitude to them here. The administrative and secretarial staff in the Graduate Institute of the National Tsing Hua University have given me much help, especially all the directors and Miss Y M Chang (張月梅). I record my thanks to them here.

Moreover, I have to thank my parents. They have always expressed their full support for my work. That this book could be finished at all owes much to their encouragement and support; but I have seldom done my filial duty. I therefore dedicate this book (Chinese edition) to my parents.

This book has much room for improvement. I hope the reader will not hesitate to give his views.

*Spring 1982*

S K Ma

#### **Publisher's Acknowledgement**

The publisher is deeply grateful to Professor M K Fung for translating the Chinese text and to K Young, J Chen, K C Chang, C H Lai, J Martinez, Y Koh and J Tay for checking the translation and galley proofs. Since Professor Ma passed away before the English edition could be completed their cooperation with us in this effort was indispensable. We hope that the spirit and depth of Professor Ma's views on Statistical Mechanics are well communicated in this book.