Thermal Physics

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Thermodynamics and Statistical Mechanics for Scientists and Engineers

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Dedication

To Care ....

who cared about every word
and helped me write what I meant to say
rather than what I had written

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About the Cover

To represent the many scientists who have made major contributions to the foundations of thermodynamics and statistical mechanics, the cover of this book depicts four significant scientists along with some equations and graphs associated with each of them.

- James Clerk Maxwell (1831-1879) for his work on thermodynamics and especially the kinetic theory of gases, including the Maxwell relations derived from perfect differentials and the Maxwell-Boltzmann Gaussian distribution of gas velocities, a precursor of ensemble theory (see Sections 5.2, 19.4, and 20.1).
- Ludwig Boltzmann (1844-1906) for his statistical approach to mechanics of many particle systems, including his Eta function that describes the decay to equilibrium and his formula showing that the entropy of thermodynamics is proportional to the logarithm of the number of microscopic realizations of a macrosystem (see Chapters 15–17).
- J. Willard Gibbs (1839-1903) for his systematic theoretical development of the thermodynamics of heterogeneous systems and their interfaces, including the definition of chemical potentials and free energy that revolutionized physical chemistry, as well as his development of the ensemble theory of statistical mechanics, including the canonical and grand canonical ensembles. The contributions of Gibbs are ubiquitous in this book, but see especially Chapters 5–8, 12–14, 17, 20, and 21.
- Max Planck (1858-1947, Nobel Prize 1918) for his quantum hypothesis of the energy of cavity radiation (hohlraum blackbody radiation) that connected statistical mechanics to what later became quantum mechanics (see Section 18.3.2); the Planck distribution of radiation flux versus frequency for a temperature 2.725 K describes the cosmic microwave background, first discovered in 1964 as a remnant of the Big Bang and later measured by the COBE satellite launched by NASA in 1989.

The following is a partial list of many others who have also made major contributions to the field, all deceased. Recipients of a Nobel Prize (first awarded in 1901) are denoted by the letter "N" followed by the award year. For brief historical introductions to thermodynamic and statistical mechanics, see Cropper [99, pp. 41-136] and Pathria and Beale [9, pp. xxi-xxvi], respectively. The scientists are listed in the order of their year of birth:

Sadi Carnot (1796-1832); Julius von Mayer (1814-1878); James Joule (1818-1889); Hermann von Helmholtz (1821-1894); Rudolf Clausius (1822-1888); William Thomson, Lord Kelvin (1824-1907); Johannes van der Waals (1837-1923, N1910); Jacobus van't Hoff (1852-1911, N1901); Wilhelm Wien (1864-1928, N1911); Walther Nernst (1864-1941, N1920); Arnold Sommerfeld (1868-1951); Théophile de Donder (1872-1957); Albert

Einstein (1879-1955, N1921); Irving Langmuir (1881-1957, N1932); Erwin Schrödinger (1887-1961, N1933); Satyendra Bose (1894-1974); Pyotr Kapitsa (1894-1984, N1978); William Giauque (1895-1982, N1949); John van Vleck (1899-1980, N1977); Wolfgang Pauli (1900-1958, N1945); Enrico Fermi (1901-1954, N1938); Paul Dirac (1902-1984, N1933); Lars Onsager (1903-1976, N1968); John von Neumann (1903-1957); Lev Landau (1908-1968, N1962); Claude Shannon (1916-2001); Ilya Prigogine (1917-2003, N1977); Kenneth Wilson (1936-2013, N1982).

Preface

This book is based on lectures in courses that I taught from 2000 to 2011 in the Department of Physics at Carnegie Mellon University to undergraduates (mostly juniors and seniors) and graduate students (mostly first and second year). Portions are also based on a course that I taught to undergraduate engineers (mostly juniors) in the Department of Metallurgical Engineering and Materials Science in the early 1970s. It began as class notes but started to be organized as a book in 2004. As a work in progress, I made it available on my website as a pdf, password protected for use by my students and a few interested colleagues.

It is my version of what I learned from my own research and self-study of numerous books and papers in preparation for my lectures. Prominent among these sources were the books by Fermi [1], Callen [2], Gibbs [3, 4], Lupis [5], Kittel and Kroemer [6], Landau and Lifshitz [7], and Pathria [8, 9], which are listed in the bibliography. Explicit references to these and other sources are made throughout, but the source of much information is beyond my memory.

Initially it was my intent to give an integrated mixture of thermodynamics and statistical mechanics, but it soon became clear that most students had only a cursory understanding of thermodynamics, having encountered only a brief exposure in introductory physics and chemistry courses. Moreover, I believe that thermodynamics can stand on its own as a discipline based on only a few postulates, or so-called laws, that have stood the test of time experimentally. Although statistical concepts can be used to motivate thermodynamics, it still takes a bold leap to appreciate that thermodynamics is valid, within its intended scope, independent of any statistical mechanical model. As stated by Albert Einstein in Autobiographical Notes (1946) [10]:

> *"A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made on me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown."*

Of course thermodynamics only allows one to relate various measurable quantities to one another and must appeal to experimental data to get actual values. In that respect, models based on statistical mechanics can greatly enhance thermodynamics by providing values that are independent of experimental measurements. But in the last analysis, any model must be compatible with the laws of thermodynamics in the appropriate limit of

sufficiently large systems. Statistical mechanics, however, has the potential to treat smaller systems for which thermodynamics is not applicable.

Consequently, I finally decided to present thermodynamics first, with only a few connections to statistical concepts, and then present statistical mechanics in that context. That allowed me to better treat reversible and irreversible processes as well as to give a thermodynamic treatment of such subjects as phase diagrams, chemical reactions, and anisotropic surfaces and interfaces that are especially valuable to materials scientists and engineers.

The treatment of statistical mechanics begins with a mathematical measure of disorder, quantified by Shannon in the context of information theory. This measure is put forward as a candidate for the entropy, which is formally developed in the context of the microcanonical, canonical, and grand canonical ensembles. Ensembles are first treated from the viewpoint of quantum mechanics, which allows for explicit counting of states. Subsequently, classical versions of the microcanonical and canonical ensembles are presented in which integration over phase space replaces counting of states. Thus, information is lost unless one establishes the number of states to be associated with a phase space volume by requiring agreement with quantum treatments in the limit of high temperatures. This is counter to the historical development of the subject, which was in the context of classical mechanics. Later in the book I discuss the foundation of the quantum mechanical treatment by means of the density operator to represent pure and statistical (mixed) quantum states.

Throughout the book, a number of example problems are presented, immediately followed by their solutions. This serves to clarify and reinforce the presentation but also allows students to develop problem-solving techniques. For several reasons I did not provide lists of problems for students to solve. Many such problems can be found in textbooks now in print, and most of their solutions are on the internet. I leave it to teachers to assign modifications of some of those problems or, even better, to devise new problems whose solutions cannot yet be found on the internet.

The book also contains a number of appendices, mostly to make it self-contained but also to cover technical items whose treatment in the chapters would tend to interrupt the flow of the presentation.

I view this book as an intermediate contribution to the vast subjects of thermodynamics and statistical mechanics. Its level of presentation is intentionally more rigorous and demanding than in introductory books. Its coverage of statistical mechanics is much less extensive than in books that specialize in statistical mechanics, such as the recent third edition of Pathria's book, now authored by Pathria and Beale [9], that contains several new and advanced topics. I suspect the present book will be useful for scientists, particularly physicists and chemists, as well as engineers, particularly materials, chemical, and mechanical engineers. If used as a textbook, many advanced topics can be omitted to suit a one- or two-semester undergraduate course. If used as a graduate text, it could easily provide for a one- or two-semester course. The level of mathematics needed in most parts of the book is advanced calculus, particularly a strong grasp of functions of several

variables, partial derivatives, and infinite series as well as an elementary knowledge of differential equations and their solutions. For the treatment of anisotropic surfaces and interfaces, necessary relations of differential geometry are presented in an appendix. For the statistical mechanics part, an appreciation of stationary quantum states, including degenerate states, is essential, but the calculation of such states is not needed. In a few places, I use the notation of the Dirac vector space, bras and kets, to represent quantum states, but always with reference to other representations; the only exceptions are Chapter 26, Quantum Statistics, where the Dirac notation is used to treat the density operator, and Appendix I, where creation and annihilation operators are treated.

I had originally considered additional information for this book, including more of my own research on the thermodynamics of inhomogeneously stressed crystals and a few more chapters on the statistical mechanical aspects of phase transformations. Treatment of the liquid state, foams, and very small systems were other possibilities. I do not address many-body theory, which I leave to other works. There is an introduction to Monte Carlo simulation at the end of Chapter 27, which treats the Ising model. The renormalization group approach is described briefly but not covered in detail. Perhaps I will address some of these topics in later writings, but for now I choose not to add to the already considerable bulk of this work.

Over the years that I shared versions of this book with students, I received some valuable feedback that stimulated revision or augmentation of topics. I thank all those students. A few faculty at other universities used versions for self-study in connection with courses they taught, and also gave me some valuable feedback. I thank these colleagues as well. I am also grateful to my research friends and co-workers at NIST, where I have been a consultant for nearly 45 years, whose questions and comments stimulated a lot of critical thinking; the same applies to many stimulating discussions with my colleagues at Carnegie-Mellon and throughout the world. Singular among those was my friend and fellow CMU faculty member Prof. William W. Mullins who taught me by example the love, joy and methodologies of science. There are other people I could thank individually for contributing in some way to the content of this book but I will not attempt to present such a list. Nevertheless, I alone am responsible for any misconceptions or outright errors that remain in this book and would be grateful to anyone who would bring them to my attention.

In bringing this book to fruition, I would especially like to thank my wife Carolyn for her patience and encouragement and her meticulous proofreading. She is an attorney, not a scientist, but the logic and intellect she brought to the task resulted in my rewriting a number of obtuse sentences and even correcting a number of embarrassing typos and inconsistent notation in the equations. I would also like to thank my friends Susan and John of Cosgrove Communications for their guidance with respect to several aesthetic aspects of this book. Thanks are also due to the folks at my publisher Elsevier: Acquisitions Editor Dr. Anita Koch, who believed in the product and shepherded it through technical review, marketing and finance committees to obtain publication approval; Editorial Project Manager Amy Clark, who guided me though cover and format design as

well as the creation of marketing material; and Production Project Manager Paul Prasad Chandramohan, who patiently managed to respond positively to my requests for changes in style and figure placements, as well as my last-minute corrections. Finally, I thank Carnegie Mellon University for providing me with an intellectual home and the freedom to undertake this work.

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