

Introduction: Theories of Thermodynamics, Kinetic Theory and Statistical Mechanics

Despite the lack of a reliable atomic theory of matter, the science of Thermodynamics flourished in the 19th century. Among the famous thinkers it attracted, one notes William Thomson (Lord Kelvin) after whom the temperature scale is named, and James Clerk Maxwell. The latter's many contributions include the "distribution function" and some very useful differential "relations" among thermodynamic quantities (as distinguished from his even more famous "equations" in electrodynamics). The Maxwell relations set the stage for our present view of thermodynamics as a science based on function theory while grounded in experimental observations.

The kinetic theory of gases came to be the next conceptual step. Among pioneers in this discipline one counts several unrecognized geniuses, such as J. J. Waterston who — thanks to Lord Rayleigh — received posthumous honors from the very same Royal Society that had steadfastly refused to publish his works during his lifetime. Ludwig Boltzmann committed suicide on September 5, 1906, depressed — it is said — by the utter rejection of his atomistic theory by such colleagues as Mach and Ostwald. Paul Ehrenfest, another great innovator, died by his own hand in 1933. Among 20th century scientists in this field, a sizable number have met equally untimely ends. So "*now*", (here we quote from a well-known and popular text^a) "it is *our* turn to study statistical mechanics".

The postulational science of Statistical Mechanics — originally introduced to justify and extend the conclusions of thermodynamics but nowadays extensively studied and used on its own merits — is entirely a product of the 20th century. Its founding fathers include Albert Einstein (who, among his many other contributions, made sense out of Planck's Law) and J. W. Gibbs, whose formulations of phase space and entropy basically

^aD. H. Goodstein, *States of Matter*, Dover, New York, 1985.

anticipated quantum mechanics. Many of the pioneers of quantum theory also contributed to statistical mechanics. We recognize this implicitly whenever we specify particles that satisfy “Fermi–Dirac” or “Bose–Einstein” statistics, or when we solve the “Bloch equation” for the density matrix, or when evaluating a partition function using a “Feynman path integral”.

In its most simplistic reduction, *thermodynamics* is the study of mathematical identities involving partial derivatives of well defined functions. These relate various macroscopic properties of matter: pressure, temperature, density, magnetization, etc., to one another. Phase transitions mark the discontinuities of one or more of these functions and serve to separate distinct regions (e.g. vapor from solid) in the variables’ phase space. *Kinetic theory* seeks to integrate the equations of motion of a many-body system starting from random initial conditions, thereby to construct the system’s thermodynamic properties. Finally, *statistical mechanics* provides an axiomatic foundation for the preceding while allowing a wide choice of convenient calculational schemes.

There is no net flow of matter nor of charged particles in thermodynamic equilibrium. Away from equilibrium but in or near *steady state*, the *Boltzmann equation* (and its quantum generalizations by Kubo and others) seeks to combine kinetic theory with statistical mechanics. This becomes necessary in order to explain and predict transport phenomena in a non-ideal medium, or to understand the evolution to equilibrium when starting from some arbitrary initial conditions. It is one of the topics covered in the present text.

Any meaningful approach revolves about taking N , the number of distinct particles under consideration, to the limit $N \rightarrow \infty$. This is not such a dim idea in light of the fact that Avogadro’s number, $N_A = 6.022045 \times 10^{23}$ *per mole*.^b

Taking advantage of the simplifications brought about by the law of large numbers and of some 18th Century mathematics one derives the underpinnings for a science of statistical mechanics and, ultimately, finds a theoretical justification for some of the dogmas of thermodynamics. In the 11 chapters to follow we see that a number of approximate relations at small values of N become exact in the “*thermodynamic limit*” (as the procedure of taking the limit $N \rightarrow \infty$ is now known in all branches of physics, including many-body physics and quantum field theory).

^bA *mole* is the amount of a substance that contains as many elementary entities as there are carbon atoms in 12 g of Carbon 12. E.g.: 1 mole of electrons (e^-) consists of N_A particles of total mass 5.4860×10^{-4} g and total charge -96.49×10^3 coulombs.

Additionally we shall study the *fluctuations* $O(\sqrt{N})$ in macroscopic $O(N)$ *extensive* quantities, for “one person’s noise is another person’s signal”. Even when fluctuations are small, what matters most is their relation to other thermodynamic functions. For example, the “noise” in the internal energy, $\langle E^2 \rangle - \langle E \rangle^2$, is related to the same system’s heat capacity dE/dT . Additional examples come under the rubric of the “fluctuation-dissipation” theorem.

With Bose–Einstein condensation, “high”-temperature superconductivity, “*nanophysics*”, “quantum dots”, and “colossal” magnetoresistance being the order of the day, there is no lack of contemporary applications for the methods of statistical physics. However, first things first. We start the exposition by laying out and motivating the fundamentals and methodologies that have “worked” in such classic systems as magnetism and the non-ideal gas. Once mastered, these reductions should allow one to pose more contemporary questions. With the aid of newest techniques — some of which are borrowed from quantum theory — one can supply some of the answers and, where the answers are still lacking, the tools with which to obtain them. The transition from “simple” statistical mechanics to the more sophisticated versions is undertaken gradually, starting from Chapter 4 to the concluding chapters of the book. The requisite mathematical tools are supplied as needed within each self-contained chapter.

The book was based on the needs of physics graduate students but it is designed to be accessible to engineers, chemists and mathematicians with minimal backgrounds in physics. Too often physics is taught as an idealized science, devoid of statistical uncertainties. An elementary course in thermodynamics and statistical physics can remedy this; Chapters 1–4 are especially suitable for undergraduates aspiring to be theoreticians. Much of the material covered in this book is suitable for self-study but *all* of it can be used as a classroom text in a one-semester course.

Based in part on lecture notes that the author developed during a decade of teaching this material, the present volume seeks to cover many essential physical concepts and theoretical “tricks” as they have evolved over the past two centuries. Some theories are just mentioned while others are developed in great depth, the sole criterion being the author’s somewhat arbitrary opinion of the intellectual depth of the posed problem and of the elegance of its resolution. Here, function follows form.

Specifically, Chapters 1 and 2 develop the rudiments of a statistical science, touching upon metastable states, phase transitions, critical exponents and the like. Applications to magnetism and superconductivity are included *ab initio*. Chapter 3 recapitulates thermodynamics in a form

that invites comparison with the postulational statistical mechanics of Chapter 4. van der Waals gas is studied and then compared to the exactly solved Tonks' gas. Chapters 5 and 6 deal, respectively, with the quantum statistics of bosons and fermions and their various applications. We distinguish the two principal types of bosons: conserved or not. The notion of "quasiparticles" in fermion systems is stressed. We touch upon semiconductor physics and the rôle of the chemical potential $\mu(T)$ in n -type semiconductors, analyzing the case when ionized donors are incapable of binding more than one excess electron due to 2-body forces. Chapter 7 presents the kinetic theory of dilute gases. Boltzmann's H -function is used to compute the approach to thermodynamic equilibrium and his eponymous equation is transformed into an eigenvalue problem in order to solve for the dispersion and decay of sound waves in gases.

Chapter 8 develops the concept of the transfer matrix, including an Onsager-type solution to the two-dimensional Ising model. Exact formulas are used to calculate the critical exponents of selected second-order phase transitions. The concept of "frustration" is introduced and the transfer matrix of the "fully frustrated" two-dimensional Ising model is diagonalized explicitly. A simplified model of fracture, the "zipper", is introduced and partly solved; in the process of studying this "classical" system, we learn something new about the equations of continuity in quantum mechanics!

The subsequent and last chapters highlight some of the most remarkable achievements of the recent decades: the successful application of the renormalization group approach of quantum field theory to the study of second-order phase transitions, and the numerical — essentially experimental — solution of complex models, using a random approach denoted "Monte-Carlo" and inspired by what is arguably the gambling capital of the world.

The last chapter concerns advanced techniques: Doi's field-theoretic approach to diffusion-limited reactions or processes, Greens function approach to the many-body problem at finite temperature is another. As illustrations, we work out the spectrum of several special models including that of a perfectly random Hamiltonian.

Additional models and calculations have been relegated to the numerous problems scattered throughout the text, where you, the reader, can test your mastery of the material. But despite coverage of a wealth of topics this book remains incomplete, as any text of normal length and scope must be. It should be supplemented by the monographs and review articles on critical phenomena, series expansions, reaction rates, exact methods, granular ma-

terials, etc., found on the shelves of even the most modest physics libraries. If used to good advantage, the present book could be a gateway to these storehouses of knowledge and research.

When this book first appeared in print a number of readers and reviewers questioned the last word in the title. Be reassured, “simple” does not mean “simple-minded.” Here is what it *does* mean: an attempt to explicate a rather unique science encompassing *all of physics* at finite T but, unlike the rest of physics, using explanations that are based not on the laws of pure motion but on those of pure chance and needing to be anchored in logic and in common sense. The greatest challenge in creating a textbook in this subject lies in choosing a few representative topics from among the many. We included conventional topics (thermodynamics, Bose gas, Fermi-Dirac statistics, etc.) along with some that were less commonplace: the concept of negative temperatures, the construction of a transfer matrix, the theory of sound-wave propagation in fluids, the nature of critical phenomena, the uses of Green functions, and many more, all the while developing the necessary mathematical tools as they became needed. Although some of this may be quite complex we strove to provide only as much detail as seemed necessary and to use only such theories and algorithms that, while adequate, felt ... simple.