

Preface

This book is intended for use both as a textbook and as a source for self-study.

As a textbook: My experience teaching courses related to Thermodynamics and Statistical Mechanics at Temple university has guided its writing. The Thermodynamics course is offered to under-graduates in their junior or senior year. These undergraduates have either a single or a double major in Physics, Biology, Chemistry, Engineering, Earth Sciences or Mathematics. The course on Statistical Mechanics is attended by graduate students in their second year. Feeling that a robust study of statistical thermodynamics appropriately belongs in a senior level graduate course, only relatively simple aspects of Statistical Mechanics are included here.

As a source for self study: Years of teaching have taught me a thing or two about what works for students and what does not. In particular, I have learned that the more attention a student pays to taking notes, the less he understands of the subject matter of the lecture being delivered. Further, I have noticed that when, a few days in advance of the delivery of the lecture, a student is provided with details of the algebra to be used, solutions to the problems to be discussed, and some brief information about the physics that is central to the lecture to be given, it obviates much of the need for note-taking during the delivery of the lecture. Another important experience that has guided the writing of this textbook is the pedagogical benefit that accrues from an occasional, quick, recapitulation of the relevant results that have already been presented in an earlier lecture. All this usually results in a better comprehension of the subject matter. Both for purposes of elucidation of the concepts introduced in the text and for providing practical problem solving support, a large number of solved examples have been included. Many of the solutions provided include greater detail than would be necessary for presentation in a lecture itself or needed by teachers or more advanced practitioners. They are there in the given form to offer encouragement and support both for self-study and indeed also to allow for fuller understanding of the subject matter. Therefore, it is as important to read through and understand these solutions as it is to learn the rest of the text.

Part of the vocabulary of thermodynamics are such terms as: A thermodynamic system; an adiabatic enclosure; an adiabatically isolated and adiabatically enclosed

system; conducting and diathermal walls; isobaric, isochoric, isothermal, quasi-static, non-quasi-static, reversible, and irreversible processes. Also, there are the concepts of thermal and thermodynamic equilibria. These terms and concepts are commonly used in thermodynamic analyses. Study of thermodynamics is greatly assisted by standard mathematical techniques. In particular, exact differentials, and some well known identities of differential calculus, are central to the theoretical description of the subject. Temperature is not only a word in normal daily use it also sits at the core of thermodynamics. The Zeroth law brings to fore one of the multivarious reasons for its relevance to the physics of thermal equilibria. The foregoing are discussed in Chap. 1.

Arguably, the emphasis on constructing simple models with the hope that they may pertain to real – and necessarily more complicated – systems of interest is unique to the discipline of Physics. Usually, these models are uncomplicated and lacking of the complexity of the real systems. But because they can often be exactly solved and understood, the hope always is that the predicted results for the model systems will give insight into the physics of real systems.

A “Perfect Gas” represents an idealized model system. The model was originally motivated by experimental observation, and constructed to understand the behavior of real gases. It has had a long and illustrious history and a great deal of success. We describe and discuss its implications in Chap. 2.

Caloric was thought to be a massless fluid whose increase warmed an object. Just like a fluid, it was thought to flow from a hot object – where there was more of it – to a cold one until the amounts of caloric in the two objects equalized. Also, like fluids, caloric could neither be created nor destroyed. Therefore, the reason a cannon muzzle got hot when it was being bored is that the chips that were created carried less caloric so more was left behind for the muzzle. While supervising the boring of a cannon, the Count Rumford of Bavaria noticed that the duller the boring bits the hotter the muzzles. In other words, less chips, but more caloric! Rumford came to the obvious conclusion: Heat energy is not exchanged by the transfer of Caloric but rather by the expenditure of work that has to be done for the drilling of the cannon. Thus work was empirically observed to be related to heat energy.

Conservation of energy is a concept as old as Aristotle.¹ The first law of thermodynamics recognizes this concept as well as Count Rumford’s observations that heat energy and work are related. If some work is performed upon adding a given amount of heat energy to a system, the portion of heat energy that is left over is called the change in the internal energy of the system. And while both the amounts of heat energy added to a system and the work done by it depend on the details of how they were carried out² the first law asserts that their difference, which is the change in the internal energy, is completely path independent. These issues are discussed in detail in Chap. 3 and solutions to many helpful problems are provided.

¹Approximately 350 BC.

²Meaning they both depend on the physical paths that were taken in executing the two processes.

Clearly, the hallmark of the first law of thermodynamics is its recognition of the path independent function: the “internal energy.” Arguably, the second law has even more to boast about: namely the identification of the state function the “entropy,” and its familial relationship with Carnot’s ideas about maximum possible efficiency of heat engines. These ideas and their various aftereffects are discussed and treated in Chap. 4.

In Chap. 5, we marry the first and the second laws of thermodynamics in a manner that achieves “a perfect union” of the two: a union that provides great insights into the workings of thermodynamics.

Many hold to the view that Johannes Diderik Van der Waals’ derivation of a possible equation of state for imperfect gases was the first ever significant contribution to predictive statistical thermodynamic. He noted that any interaction between microscopic constituents of a body must have two distinct features. Because these constituents congregate to form macroscopic entities, the overall inter-particle interaction must be attractive. Yet, because matter does condense to finite densities, at small enough distances the interaction must become strong and repulsive: meaning it must have a hard core.

He assumed both these interactions to be “short ranged.” It turns out, however, that his equation of state is somewhat more meaningful for a gas that has both a hard core – much as he assumed – but, unlike his assumption, has attractive interaction which is long ranged. These ideas as well as the many physical consequence of the Van der Waals equation of state are extensively studied and analyzed in Chap. 6.

State variables such as the volume, pressure, and temperature are easy to measure. In contrast, thermodynamic state functions such as the internal energy and the enthalpy cannot be measured by straightforward procedures. Generally, therefore, one needs to follow somewhat circuitous routes for their measurement.

The famous Gay–Lussac–Joule experiment attempted to measure the internal energy. The experiment was based on determining the amount of heat energy that is produced by free-expansion of a gas enclosed in vessels submerged in water. Unfortunately, the heat capacities of the water that needed to be used plus that of the enclosing core were vastly greater than that of the gas being used. As a result no reliable measurement could be made.

Joule and Kelvin devised an experiment that overcame this difficulty. The experiment shifted the focus from the internal energy to the enthalpy. Additionally, rather than dealing with a fixed amount of gas that is stationary, it used a procedure that involved “steady-flow.” As a result, reliable measurements could be made. The related issues and results are presented in Chap. 7.

Chapter 8 deals with: the Euler equation – namely the Complete Fundamental Equation – and its dependence on the chemical potential; the Gibbs–Duhem relation in both the energy and the entropy representations; and the three possible equations of state for the ideal gas, again in both the entropy and the energy representations.

Several important issues are broached in Chap. 9. For instance, we recall that all spontaneous processes in isolated thermodynamic systems increase their total entropy and this fact follows from the second law. Of course, spontaneous processes continue until the system ceases to change: meaning, until it achieves thermal

equilibrium. Accordingly, subject to the constraints under which the system has been maintained, and for the given value of its various extensive properties, its total entropy in thermodynamic equilibrium is the maximum possible. With this knowledge in hand, coupled with the concept of the fundamental equation, we are able to more fully examine the nature of the zeroth law.

Entropy extremum also helps explain the direction of thermodynamic motive forces. Namely: Why heat energy flows from the warm to the cold; why, at constant temperature and pressure, molecules flow from regions of higher chemical potential to those of lower chemical potential; and why the fact that if two macroscopic systems in thermal contact are placed together in an adiabatically isolated chamber, and if their total volume is constant, their chemical potentials are equal, they are at the same temperature, and they can freely affect each other's volume then the requirement that the total entropy increase in any isothermal spontaneous process ensures that the side with originally lower pressure will shrink in volume? And, why if the process is allowed to continue, the shrinking of the side with originally lower pressure, and the expansion in volume of the side with originally greater pressure, continues until the two pressures become equal?

Much like the entropy, the system energy also obeys an extremum principle. For given value of the entropy and the equilibrium values of various extensive parameters, the energy of a system is a minimum. And it turns out that the energy extremum leads to the same physical predictions that does the entropy extremum.

These extremum principles make important statements about issues that relate to intrinsic stability of thermodynamic systems. In particular, they help determine the requirement that for intrinsic stability the specific heat c_v and the isothermal compressibility χ_T must always be greater than zero.

Also discussed in Chap. 9 is the Le Châtelier principle which asserts that spontaneous processes caused by displacements from equilibrium help restore the system back to equilibrium.

The analyses presented in Chap. 9 were guided by the use of the extremum principles obeyed by the internal energy and the entropy. An important consequence of either of these two extremum principles is the occurrence of other extrema that are related to the Helmholtz potential, the Gibbs free energy, and the enthalpy. These are identified and some of their consequences predicted in Chap. 10. Legendre transformations provide an essential tool for these studies. The issue of meta-stable equilibrium is commented upon. Also Maxwell relations, the Clausius–Clapeyron and its use in the study of thermodynamic phases, and the Gibbs phase rule are described in Chap. 10.

Much of what is written in the preceding chapters has been gleaned from standard procedures which do not attempt to carry out exact numerical calculation of state functions such as the entropy and the internal energy. Indeed, the focus mainly has been on understanding the rates of change of state functions and their inter-relationships. This is because, unlike statistical mechanics, thermodynamics itself does not have any convenient method for performing these calculations.

Chapter 11 deals with Statistical Thermodynamics. Analyzed first are the classical monatomic perfect gases with constant numbers of particles. Results of

their mixing under a variety of ambient circumstances are described. Diatomic gases are treated next. Statistical mechanics of harmonic and anharmonic simple oscillators; the Langevin paramagnet; extremely relativistic ideal gas; gases with interaction; and issues relating to Mayer's cluster expansion and the Lennard–Jones potential are analyzed. Studied next are the differences between the thermodynamics of classical and the quasi-classical quantum systems. Quasi-classical analyses of diatoms with rigid bonds, and others that admit vibrational motion, are described. Nernst's heat theorem, unattainability of zero temperature, the Third Law, and indeed the concept of negative temperature are described next. Finally, the Richardson effect, the Fermi–Dirac and Bose–Einstein quantum gases, “Black Body Radiation,” and the thermodynamics of phonons are presented.

Most users of this textbook should want to read the relevant appendices. The usefulness of an appendix lies in it containing more detail than is originally provided in the body of the text. For instance, the notion that thermodynamics refers to systems that contain very large number of atoms is explained with great simplicity in appendix A: as also is the rationale for the validity of the Gaussian approximation. Appendix B is equally helpful. The re-derivation of the perfect gas law is done with straightforward argumentation: this time by using elementary statistical mechanics. Appendix C provides details of an important argument that asserts that the Carnot version of the second law leads to the Clausius version. Other appendices provide solutions to various problems that are identified in the text.

Unlike a novel, which is often read continuously – and the reading is completed within a couple of days – this book is likely to be read piecemeal – a chapter or so a week. At such slow rate of reading, it is often hard to recall the precise form of a relationship that appeared in a previous chapter or sometimes even in the earlier part of the same chapter. To help relieve this difficulty, when needed the most helpful explanation of the issue at hand is repeated briefly and the most relevant expressions are mentioned by their equation numbers. Throughout the book, for efficient reading, most equations are numbered in seriatim. When needed, they can be accessed quickly.

A fact well known to researchers is that when a physics problem is analyzed in more ways than one, its understanding is often greatly enhanced. Similar improvement in comprehension is achieved when students are also provided access to alternate, yet equivalent, explanations of the subject matter relating to important physical concepts. To this end, effort has been made to provide – wherever possible – additional, alternate solutions to given problems and also to the derivation of noteworthy physical results. Occasionally, brief historical references have also been included in the text.

Most of the current knowledge of thermodynamics is much older than the students who study it. Numerous books have been written on the subject. While the current book owes greatly to three well known texts on thermodynamics³ and

³Namely: Herbert B. Callen, John Wiley Publishers (1960); D. ter Haar and H. Wergeland, Addison-Wesley Publishing Company (1966); F. W. Sears and G. L. Salinger, Addison-Wesley

one on statistical mechanics,⁴ its import is different: it is offered as much for use in formal lectures as for self-study.^{5,6}

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⁴Namely: R. K. Pathria, Pergamon Press (1977).

⁵Callen, Herbert B (1919)–(5/22/1993).

⁶ter Haar, Dirk (4/22/1919)–(9/3/2002).

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