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M. Scott Shell
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1 Introduction and guide for this text

Thermodynamics is a remarkable subject, both in its pervasiveness throughout the pure and engineering sciences, and in the striking simplicity and elegance of its principles. Indeed, it is hard to underestimate the significance of thermodynamics to virtually any physical problem of interest, even if its role appears only indirectly through derivative theories or models. As a testament to its importance, Einstein made the rather potent statement that thermodynamics 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.”

At the same time, thermodynamics can be surprisingly difficult to grasp at a fundamental level, even for the experienced student. Unlike many other advanced scientific subjects, its main challenges are not mathematical in nature; a working knowledge of multivariate calculus is usually quite sufficient. Instead, the most difficult aspects of thermodynamics are its conceptual underpinnings. Students often struggle with the seemingly simple task of how to begin thinking about a problem, finding it difficult to answer questions such as the following. *What constitutes the system? What is constant or constrained? What thermodynamic variables are equal across a boundary? What assumptions and models are reasonable?* All of these questions precede the analytical analysis and are concerned with how to transform the physical problem into a mathematical one. When this is done, the solutions often present themselves in a rather straightforward manner, at least for an introductory treatment.

It is exactly these conceptual ideations on which this book is focused. This text presents an advanced undergraduate or early graduate-level overview of thermodynamics aimed at students in chemical science and engineering. It is designed to provide a fundamental understanding of thermodynamic principles that emphasizes general concepts and approaches, rather than notations, mathematical frameworks, or solution strategies for specific kinds of applications. It adopts the philosophy that the most important step a student can take in this area is to gain basic physical intuition and confidence in problem analysis and model-development. To some extent, this book is designed to “fill in the gaps” from earlier, introductory exposure to the subject and to help students see and become comfortable with the “big picture.” That being said, it is assumed that the reader is equipped with some prior exposure and training in the following areas.

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- *Multivariate differential and integral calculus*: familiarity with total differentials, partial derivatives, single- and multiple-variable integrations, and solutions to very simple differential equations.
- *Basic statistics and probability*: familiarity with the concepts of probability, probability distributions (including multivariate), and combinatorics.
- *Introductory exposure to thermodynamic concepts and terminology*: familiarity with the concepts of a system, surroundings, boundary, absolute temperature, pressure, heat, work, and processes.

It is very likely that any reader with at least three or four years of undergraduate coursework in physics, chemistry, or engineering will be sufficiently prepared for this book. Regardless, most of the requisite background material is reviewed or explained with examples in an as-you-go manner.

The most distinguishing feature of this text is that it integrates macroscopic principles (classical thermodynamics) and molecular aspects of thermodynamics (statistical mechanics) throughout. This constitutes a different perspective than many traditional treatments of the material that begin purely at the macroscopic level with the so-called *postulatory approach*. The latter gives a beautiful formulation of classical thermodynamics that makes no reference to the molecular world and hence is independent of the particular nature of microscopic interactions. Instead, the postulatory approach proposes several general principles, reinforced many times over by empirical observation, with which any problem can be analyzed. In other words, that approach begins *a priori* with the laws of thermodynamics. Although they may be phrased in different ways, the following list gives some usual possibilities for the laws.

1. No process can operate in such a way as to create or destroy energy.
   The total energy of an isolated system is constant. If the internal energy of a closed system changes, the difference must exactly equal the sum of the heat added and work done on it: $dE = \delta Q + \delta W$.
2. No process can operate so as to completely convert the heat absorbed by a system into usable work.
   Systems have a quantity called the entropy that is a function of state and that can be measured using reversible heat transfers: $dS = \delta Q_{\mathrm{rev}}/T$. In an isolated system, the entropy of spontaneous processes can only increase with time.
3. No process can operate so as to bring a system to absolute zero in a finite number of steps and in finite time.
   The entropy of all perfect, pure, monatomic crystalline substances at absolute zero is zero.

The brilliance of these statements is that, despite their simplicity, they have profound implications that can be studied in great mathematical detail for every physical process. Furthermore, they require no understanding of molecular interactions or the fundamental theory thereof.

Unfortunately, while the postulatory formulation is often greatly esteemed by experienced scientists, it can be a challenging starting point for the early learner. The main problem is that it requires students to merely accept these statements, without explanation as to how they connect to molecular principles that they surely have seen in other courses. *What really is the entropy and why does it exist?* The gap between the atomic world and thermodynamics often leaves students feeling unsatisfied, confused, lacking intuition, and missing the big picture.

This book therefore takes a different, *integrated approach* to teaching thermodynamics that blends molecular and statistical-mechanical concepts with the exposition of the classical laws. It attempts to be bottom-up rather than top-down by first presenting and then rationalizing ideas on the basis of atomic-scale interactions. In this sense, it aims to give the reader some feeling for the *why* of thermodynamics. Of course, this approach itself is not devoid of postulates. To begin, one must accept some level of atomic theory, whether quantum or classical or other. Moreover, ultimately the second law requires the *equal a priori* assumption that is the foundation of statistical mechanics, as discussed in Chapter 4. In this sense the approach taken by this text is motivated on pedagogical grounds, not scientific ones. After understanding the material, therefore, the reader is highly encouraged to revisit the postulatory presentation to appreciate the generality of thermodynamics as an empirical natural science that is independent of the microscopic world.

The reader should be cautioned that a deep understanding of thermodynamics does not simply evolve from the page, but rather requires a concerted effort to explore the material outside of the main narrative. Some recommendations for working through this text are the following:

- **Pay particular attention to general, broad concepts.** The most important ones are highlighted for you in gray call-out boxes. Ask yourself the following questions. *Does this make sense intuitively? Does this make sense mathematically?* Challenge yourself to understand and apply the ideas, initially in very simple examples. Make sure that you feel comfortable with the concepts before proceeding too far ahead, since it is easy to become lost. Check yourself with questions in the *Conceptual and thought problems* section at the end of each chapter.
- **Work through the end-of-chapter problems.** One simply cannot appreciate thermodynamics without tackling actual problems. If you are reading this text outside of class, a suggested course of study is the end-of-chapter problems that are indicated with boxed numbers. You will likely struggle through them, and it is important that you do so! It is through this process of struggle that subtleties bubble to the surface. This book has been written so that many important results and implications are explicitly left for you to discover in this engaged, problem-driven manner. Note that some chapters have many more problems than others, and this is because they are natural synthesis points for incorporating earlier material.
- **Think in terms of functions and variables, not values.** Students often become complacent with plugging numbers into off-the-shelf equations. This is a *value*-focused way to solve problems, and it is entirely the wrong way to understand thermodynamics. Instead, much of the beauty of this subject is that properties are interrelated through a systematic calculus of functions. Indeed, any equilibrium

property is a function of state and thus also a *mathematical* function. This means that such properties have multiple independent variables and partial derivatives. At first it may seem unsettling to consider temperature as a function, for example $T(E, V, N)$, but keep in mind that its behavior is no different than that of the generic $f(x, y, z)$.

- **Always solve problems from general principles, not specialized equations.** One of the attractive features of thermodynamics is that there are just a few fundamental equations from which essentially all other results can be derived. Therefore, you should not try to memorize every equation, but instead strive to be able to quickly pinpoint the underlying assumptions so that you would be able to re-derive the key ones in isolation. Throughout this book, the most important equations are numbered in bold.

Finally, the reader is encouraged to explore other texts as a means to broaden understanding and clarify confusing points. Some especially useful texts are referenced at the end of this chapter. In particular, many parts of the present book follow closely and were inspired by the brilliant texts of Denbigh, Hill, and McQuarrie. While these seminal works have a less modern tone, they present the material with great care and in significantly greater depth. In addition, the text by Dill gives a terrific introduction to thermodynamics suited to a more general audience, and it addresses many background concepts that are not covered in detail by the present work.

FURTHER READING

Highly recommended supplementary reading for early graduate-level students in the chemical sciences and engineering

K. Denbigh, *The Principles of Chemical Equilibrium*, 4th edn. New York: Cambridge University Press (1981).

K. Dill and S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, 2nd edn. New York: Garland Science (2010).

T. L. Hill, *An Introduction to Statistical Thermodynamics*. Reading, MA: Addison-Wesley (1960); New York: Dover (1986).

D. A. McQuarrie, *Quantum Chemistry*. Mill Valley, CA: University Science Books (1983).

D. A. McQuarrie, *Statistical Mechanics*. Sausalito, CA: University Science Books (2000).

Also recommended

H. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 3rd edn. New York: Wiley (1985).

D. Chandler, *Introduction to Modern Statistical Mechanics*. New York: Oxford University Press (1987).

J. R. Elliot and C. T. Lira, *Introductory Chemical Engineering Thermodynamics*, 2nd edn. Upper Saddle River, NJ: Prentice Hall (2012).

J. Israelachvili, *Intermolecular and Surface Forces*, 3rd edn. Burlington, MA: Academic Press (2011).

C. Kittel and H. Kroemer, *Thermal Physics*. New York: W. H. Freeman (1980).

A. Z. Panagiotopoulos, *Essential Thermodynamics*. Princeton, NJ: Drios Press (2011).

J. M. Smith, H. V. Ness, and M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 7th edn. New York: McGraw-Hill (2005).

J. W. Tester and M. Modell, *Thermodynamics and Its Applications*, 3rd edn. Upper Saddle River, NJ: Prentice Hall (1997).

For this chapter

A. Einstein, "Autobiographical notes" in *Albert Einstein: Philosopher-Scientist*, P. A. Schlipp, ed. Evanston, IL: Library of Living Philosophers (1949).

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2 Equilibrium and entropy

2.1 What is equilibrium?

At its most basic level, the subject of thermodynamics is the study of the properties of systems and substances at *equilibrium*. What do we mean by equilibrium? A simple way of thinking about this concept is that it represents the state where time is an irrelevant variable.

We can think of **thermodynamic equilibrium** as the condition where the following statements hold.

(1) The properties of a system do not change with time.
(2) The properties of a system do not depend on how it was prepared, but instead depend only on the current conditions of state, that is, a short list of parameters such as temperature, pressure, density, and composition that summarize the current equilibrium. A system brought to a specific equilibrium state always behaves identically, and such states are *history-independent.* The notion of history-independence is more restrictive than the statement that properties do not change with time. Indeed, history-independence is an important factor of *thermodynamic* equilibrium.
(3) The properties of a large number of copies of the same system at the same state conditions are identical, irrespective of whether or not each copy had a distinct preparation and history.

On the other hand, one might question whether these statements are compatible with the molecular nature of reality. Do not the molecules in a glass of water rotate and move about? Are not their positions, orientations, and velocities constantly changing? How then can the glass of water ever be at equilibrium, given this ongoing evolution?

The resolution to this seeming conundrum is that thermodynamic equilibrium is concerned with certain *average* properties that become time-invariant. By average, we mean two things. First, these properties are measured at a bulk, *macroscopic* level, and are due to the interactions of many molecules. For example, the pressure that a gas exerts on the interior of a container is due to the average rate of collisions and momentum transfer of many molecules with a vessel wall. Such macroscopic properties are typically averaged over very many ($\sim10^{23}$) molecular interactions.

Second, equilibrium properties are measured over some window of time that is much greater than the time scales of the molecular motion. If we could measure the instantaneous density of a gas at any single moment, we would find that some very small, microscopic regions of space would have fewer molecules and hence lower density than others, while some spaces would have more molecules and higher density, due to random atomic motions. However, measured over a time scale greater than the average collision time, the time-averaged density would appear uniform in space.

In fact, the mere concept of equilibrium requires there to be some set of choices that a system can make in response to environmental conditions or perturbations. These choices are the kinds of positions, orientations, and velocities experienced by the constituent molecules. Of course, a system does not make a literal, cognitive choice, but rather the behavior of the molecules is determined naturally through their energetic interactions with each other and the surroundings.

So far, we have hinted at a very important set of concepts that involve two distinct perspectives of any given system.

> **Macroscopic** properties are those that depend on the bulk features of a system of many molecules, such as the pressure or mean density. **Microscopic** properties are those that pertain to individual molecules, such as the position and velocity of a particular atom. The equilibrium properties of a system measured at a macroscopic level actually derive from the **average** behavior of many molecules (typically $\sim 10^{23}$), over periods of time.

The connection between macroscopic equilibrium properties and the molecular nature of reality is the theme of this book, and the basis of thermodynamics. In particular, we will learn exactly how to connect averages over molecular behavior to bulk properties, a task that forms the basis of statistical mechanics. Moreover, we will learn that, due to the particular ways in which molecules interact, the bulk properties that emerge when macroscopic amounts of them interact are subject to a number of simple laws, which form the principles of classical thermodynamics.

Note that we have not defined thermodynamics as the study of heat and energy specifically. In fact, equilibrium is more general than this. Thermodynamics deals with heat and energy because these are mechanisms by which systems and molecules can interact with one another to come to equilibrium. Other mechanisms include the exchange of mass (e.g., diffusion) and the exchange of volume (e.g., expansion or contraction).

2.2 Classical thermodynamics

Classical thermodynamics provides laws and a mathematical structure that govern the behavior of bulk, macroscopic systems. While its basic principles ultimately emerge from molecular interactions, classical thermodynamics makes no reference to the atomic scale and, in fact, its core was developed before the molecular nature of matter was generally accepted. That is to say, classical thermodynamics provides a set of laws and relationships exclusively among macroscopic properties, and can be developed entirely on the basis of just a few postulates without consideration of the molecular world.

In our discussion of equilibrium above, we did not say anything about the concepts of heat, temperature, and entropy. Why? These are all macroscopic variables that are a *consequence* of equilibrium, and do not quite exist at the level of individual molecules. For the most part, these quantities have real significance only in systems containing numerous molecules, or in systems in contact with “baths” that themselves are macroscopically large. In other words, when large numbers of molecules interact and come to equilibrium, it turns out that there are new relevant quantities that can be used to describe their behavior, just as the quantities of momentum and kinetic energy emerge as important ways to describe mechanical collisions.

The concept of *entropy*, in particular, is central to thermodynamics. Entropy tends to be confusing because it does not have an intuitive connection to mechanical quantities, such as velocity and position, and because it is not conserved, like energy. Entropy is also frequently described using qualitative metrics such as “disorder” that are imprecise and difficult to interpret in practice. Not only do such descriptions do a terrible disservice to the elegant mathematics of thermodynamics, but also the notion of entropy as “disorder” is sometimes outright wrong. Indeed, there are many counter-examples where entropy increases while subjective interpretations would consider order to increase as well. Self-assembly processes are particularly prominent cases, such as the tendency of surfactants to form micelles and vesicles, or the autonomous hybridization of complementary DNA strands into helical structures.

In reality, entropy is not terribly complicated. It is simply a mathematical *function* that emerges naturally for equilibrium in *isolated systems*, that is, systems that cannot exchange energy or particles with their surroundings and that are at fixed volume. For a single-component system, that function is

$$S = S(E, V, N) \tag{2.1}$$

which states that the entropy is dependent on three macroscopic quantities: the total internal energy of the system E, the total volume of the system V, and the number of particles (molecules or atoms) N. The internal energy stems from all of the molecular interactions present in the system: the kinetic energies of all of the molecules plus the potential energies due to their interactions with each other and with the container walls. For multicomponent systems, one incurs N additional variables for each species,

$$S = S(E, V, N_1, N_2, N_3, \ldots) \tag{2.2}$$

At this point, let us think of the entropy not as some mysterious physical quantity, but simply as a mathematical function that exists for all systems and substances at equilibrium. We do not necessarily know the analytical form of this function, but nonetheless such a function exists. That is, for any one system with specific values of E, V, and N, there is a unique value of the entropy.

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The reason why the entropy depends on these particular variables relates, in part, to the fact that E, V, and N are all rigorously constant for an isolated system due to the absence of heat, volume, and mass transfer. What about non-isolated systems? In those cases, we have to consider the total entropy of the system of interest *plus* its surroundings, which together constitute a net isolated system. We will perform such analyses later on, but will continue to focus on isolated systems for the time being.

The specific form of this entropy function is different for every system, irrespective of whether it is a pure substance or mixture. However, *all* entropy functions have some shared properties, and these common features underlie the power of thermodynamics. These properties are mathematical in nature.

(1) **Partial derivatives**

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \text{ where } T \text{ is the absolute temperature}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \text{ where } P \text{ is the absolute pressure}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \text{ where } \mu \text{ is the chemical potential}$$

(2) **Extensivity**

$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$ where λ is an arbitrary positive real number

(3) **Concavity**

$$\left(\frac{\partial^2 S}{\partial X^2}\right)_{Y,Z} \leq 0 \text{ where } X \text{ is } E, V, \text{ or } N, \text{ and } Y \text{ and } Z \text{ are the remaining two}$$

Properties (2) and (3) arise from the nature of molecular interactions in large systems, and two problems at the end of Chapter 3 consider a simple approach to their derivation. For now, the most important of these common features is the partial derivatives of property (1). Instead of listing these separately as above, we often write them using the total differential,

$$dS = \frac{1}{T}\,dE + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN \qquad \textbf{(2.3)}$$

The differential form simply summarizes the set of partials. Strictly speaking, the variables T, P, and μ are not independent in the entropy function (like E, V, and N), but rather are themselves functions that stem from the derivatives of S,

$$T(E, V, N),\ P(E, V, N),\ \mu(E, V, N) \qquad (2.4)$$

This result, of course, is a basic mathematical fact. The differential form for the entropy can be rearranged into an expression for the energy,

$$dE = T\,dS - P\,dV + \mu\,dN \qquad \textbf{(2.5)}$$

Both forms imply the same relationships. Equations (2.3) and (2.5) are simple transformations of each other, equivalent to inverting the function $S(E, V, N)$ to $E(S, V, N)$.

That is, (2.5) implies a function that returns the equilibrium internal energy corresponding to a specified entropy (and V and N). This form will become more useful and intuitive later on, but it contains exactly the same information. In fact, both of these differential forms are called the *fundamental equation*, being labeled the entropy and energy versions, respectively. For multicomponent systems, there is a distinct chemical potential corresponding to each particle number. In this case, the fundamental equations are

$$dS = \frac{1}{T}\,dE + \frac{P}{T}\,dV - \sum_i \frac{\mu_i}{T}\,dN_i \qquad \textbf{(2.6)}$$

$$dE = T\,dS - P\,dV + \sum_i \mu_i\,dN_i \qquad \textbf{(2.7)}$$

The entropy is the basic function describing equilibrium. It is natural to wonder what this means. What does one do with the entropy function? The relationships we have described thus far already tell us a few important facts. First, they indicate what is necessary to determine the equilibrium state of a system.

Only three pieces of information are necessary to specify the entropy for a single-component system, E, V, and N. By extension, only three pieces of information are necessary to completely specify the **equilibrium state** of the system. For a C-component system, we need $C + 2$ pieces of information. As we will learn later, intensive properties that do not scale with the size of the system require one less piece of information. That information is essentially the system size.

Moreover, the common properties of the entropy provide a way to interrelate thermodynamic properties.

We can calculate the pressure, temperature, and chemical potential from the entropy function if we know a system's E, V, and N, simply by evaluating the three partial derivatives at these values.

Alternatively, if we knew T, V, and N, we could find the energy of the system as the value that satisfied $(\partial S/\partial E)_{V,N} = 1/T$. Note here that E appears, along with V and N, as the point at which the derivative is evaluated. A similar construction can be made with the other partial derivatives.

A key idea is that we can relate the entropy to measurable properties like the temperature or heat capacity by exploiting connections to its derivatives. In fact, often we can use data measured in experiments to back-out the form of the entropy through integration. For example, if we integrate the energy partial derivative, we find

$$S = \int \frac{1}{T(E,V,N)}\,dE + f(V,N) \qquad (2.8)$$