# THERMODYNAMICS AND STATISTICAL PHYSICS

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# Thermodynamics and Statistical Physics

## AN ELEMENTARY TREATMENT WITH CONTEMPORARY APPLICATIONS

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# Thermodynamics and Statistical Physics

*To Jane*

# Preface

This book evolved from the author's experience in teaching a course in thermodynamics and statistical physics at Miami University to undergraduate students majoring in physics or engineering. Their previous exposure to the subject was a very brief survey in the freshman course. All portions of the text have been class tested in mimeographed note form—many of them several times.

The primary object of the book is a modest one. It is to help the student arrive at the point where his conceptions of the fundamental ideas are not only correct and precise, but where he feels comfortable with them as well. A lasting concept must seem "handmade."

The scope of the material is limited. The kinetic theory treatment stops short of the Boltzmann equation and its ramifications. The chapters on statistical mechanics make no reference to ensembles. The Boltzmann equation and ensemble theory are not elementary topics to the typical student.

The mathematical level grows in sophistication as the book progresses. Chapters 2, 10, and 14 serve to introduce and/or review various mathematical techniques.

Problems are interspersed within the text so that the student can immediately see how strong a grasp of the material he has. Numerous examples, serving various ends, are included.

References at the end of each chapter range from popular expositions suited to student use to journal articles which the instructor can digest for use as supplementary material.

My thanks are extended to the many students who made helpful suggestions. The comments of Mr. Kent Eschenberg were particularly helpful. The author is especially grateful to Professor George B. Arfken for reading the manuscript and for offering important suggestions. Above all I wish to thank my wife Jane—who was an inspiration in the writing of the book.

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# Overview

Thermodynamics and statistical physics deal with the properties of bulk matter under circumstances where the notions of temperature and heat cannot be ignored. In their present form the laws of thermodynamics and related principles comprise the essence of 150 years of experimentation and theoretical interpretation. Largely because of its empirical nature thermodynamics remains a formidable subject, especially at an elementary level. In part, the difficulty stems from the almost universal applicability of these laws. The great generality of the laws of thermodynamics requires that they be independent of the detailed workings of any particular physical system. Instead, they are based on universal principles such as the conservation of energy (first law of thermodynamics). The definitions of thermodynamic variables, though operational† and straightforward, may not convey much of a feel for the quantity so defined. This stems from the fact that such variables are nonmechanical. Historically, thermodynamics did not evolve on the basis of any atomic or mechanical model of matter which lets you see how it works.

There are four laws of thermodynamics, labeled zeroth, first, second, and third. Chronologically, only the third law is correctly numbered. The second law was formulated in 1824. The first law was stated about 20 years later. The third and zeroth laws were put forth in the 20th century.

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† An operational definition defines a quantity by describing how to measure it.

The zeroth law relates the ideas of temperature equality and thermodynamic equilibrium, without suggesting what temperature measures. The zeroth law formalizes an important experimental fact, namely, that the mutual thermodynamic equilibrium of two systems demands equality of but one property—the property we call "temperature."

The first law recognizes heat as a form of energy, and is interpreted as a statement of energy conservation.

The second law places limits on the extent to which heat may be converted into mechanical energy (work) and other useful forms. The second law is linked with the irreversibility of processes which occur spontaneously in nature, such as the flow of heat.

The third law concerns the absolute zero of temperature. One consequence of the third law is that all schemes by which absolute zero is approached suffer a severe case of diminishing returns, rendering this temperature unattainable. The third law has not discouraged low-temperature research, as temperatures within a few millionths of a degree of absolute zero have been achieved.

By contrast, statistical physics is more transparent. One starts with a microscopic model of the physical system. For example, a rarified gas is envisioned as a collection of microscopic particles (atoms or molecules) subject to the laws of mechanics. Physically observable quantities are identified as average values of certain microscopic quantities. For example, we will see that the temperature of a gas is a measure of the average kinetic energy of its molecules. One can follow the transition from the microscopic realm of atoms and molecules to the macroscopic level of bulk matter and thus develop an intuitive feeling for the quantities introduced in the process.

In general, all but the simplest models present enormously complicated mathematical problems. These complexities arise from the many-body nature of the problems. In solids, liquids, and dense gases, any given atom or molecule is most likely to be found being pushed and pulled by many neighboring atoms. Future successes in many areas of statistical physics appear to be tied to the development of improved methods for handling the many-body problem.

If the successes of statistical physics were restricted to a few idealized models, one might seriously question its methods or even its foundations. However, one overpowering result of great generality ensures our confidence in the formalism: It is possible to deduce the laws of thermodynamics by applying the principles of statistical physics. Thus statistical physics can guarantee that a Dewar of liquid helium will obey the laws of thermodynamics. In addition it provides a formalism which, in principle (but not yet fully in practice), allows us to relate the many measurable properties of bulk helium to the microscopic structure of a single helium atom.

# Chapter 1

# A Framework for Thermodynamics

## 1.1 PRELIMINARY NOTIONS

"Pick a system" is advice offered freely to physics students. The *system* is the focus of attention—that chunk of the universe whose behavior we strive to understand. The *surroundings* of a system are the remaining portions of the universe which directly affect the behavior of the system.

Favorite mechanical systems include apples which fall vertically under the influence of gravity and blocks which slide down frictionless planes. Mechanics emphasizes a system's response to external forces. A favorite system in thermodynamics and statistical physics is a rarified gas housed in a cylinder fitted with a piston. In thermodynamics we are generally concerned with the effects of energy exchanges between the system and its surroundings.

The primary virtue of systems like the falling apple and sliding block is their remarkable simplicity. By applying the principles of mechanics—Newton's laws of motion—one can predict the behavior of a falling apple. The predicted behavior is in accord with both experiment and common sense—our everyday experience. Success in dealing with such transparent problems strengthens our confidence in the principles of Newtonian mechanics.

The gas-piston system of Figure 1.1c serves the same purpose in thermodynamics; it illustrates the principles at an intuitive level. Be forewarned, however, that your deductions as beginners in thermodynamics often will not seem to be a matter of common sense. In large part the difficulty in acquiring

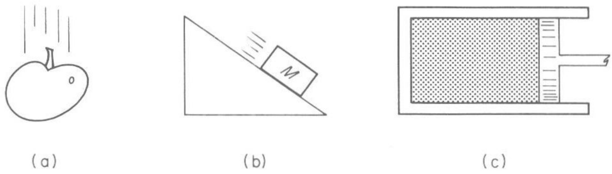


*Figure 1.1.* Favorite systems in mechanics: (a) apple falling vertically due to gravity, (b) sliding block on a frictionless plane, and in statistical physics, (c) gas–piston system.

a feel for thermodynamics stems from a lack of firsthand experience with the thermal aspects of even the simplest systems, such as gas-filled cylinders.

As a first step toward understanding the behavior of a physical system we must choose quantities which describe the system and the effects of the surroundings. If these physical quantities can be *measured*, either directly or indirectly, they are termed *macroscopic*. For example, if the system is a column of mercury in a thermometer, the density and column length, both measurable, qualify as macroscopic properties. For a confined gas, like that of Figure 1.1c, temperature, density, pressure, and volume are macroscopic variables. The macroscopic quantities used to describe the condition of a thermodynamic system are generally referred to as *thermodynamic variables*.

One may also describe a physical system at the microscopic level. This requires that we first introduce a conceptual model of the system. The model is constructed at the atomic level and employs *microscopic* variables—quantities which are not directly measurable. For example, a gas is envisioned as a collection of an enormous number of atoms which careen about wildly. The mass and kinetic energy of an atom are microscopic variables. The total mass of the gas is measurable, but not the mass of a particular atom.

Thermodynamics is formulated in terms of macroscopic variables. Kinetic theory and statistical mechanics employ microscopic variables in schemes which correlate various features of models with the macroscopic properties of physical systems.

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**1.1.1** Which of the quantities listed below are macroscopic and which are microscopic?

(a) the pressure which drives a piston in an automobile engine,
(b) the force exerted by an atom in a gas when it collides with the container wall,
(c) the wavelength of a water wave,
(d) the speed of a supersonic aircraft,
(e) the speed of a neutron in an atomic nucleus.

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Thermodynamic variables are further classified according to their dependence on the size of the system (as measured by its mass or volume). A variable is termed *extensive* if its value depends on the size of the system. A variable is referred to as *intensive* if its value is independent of the size of the system. For example, the mass of a system is an extensive property. Its mass density (mass per unit volume) is an intensive quantity.

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**1.1.2** Indicate which of the following are extensive quantities:

(a) the electrical resistance of a length of copper wire,
(b) the electrical resistivity of a length of copper wire,
(c) the kinetic energy of an automobile,
(d) the index of refraction of glass,
(e) the moment of inertia of a flywheel.

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Thermodynamic systems are classified further with respect to the exchange of matter and energy with their surroundings. In this connection it is necessary to regard heat as a form of energy which is transferred from one region to another by virtue of a temperature difference between them. A more precise and operational definition of heat is presented in Chapter 3.

An *isolated* system can exchange neither matter nor energy with its surroundings. The only candidate for a truly isolated system is the universe. However, it is not certain that all of the laws of thermodynamics apply on a cosmic scale. Despite the fact that an isolated system is an abstraction which cannot be realized in practice, a system may be regarded as isolated whenever matter and energy exchanges do not significantly disturb the processes occurring within the system. For example, a fluid in a container with rigid impermeable walls which are covered with insulation approximates an isolated system. The rigidity of the walls prevents any compressive work being done on the fluid and the insulation minimizes heat transfer. Thus no matter and a minimal amount of energy can be exchanged between the fluid and its surroundings.

A *closed* system is capable of exchanging energy, but not matter, with its surroundings. The walls of a building closely approximate a closed system. They engage in the transfer of thermal energy with the environment without an appreciable exchange of matter.

An *open* system is capable of exchanging both matter and energy with its surroundings. A living animal is a good example of an open system. Matter is exchanged with the surroundings by the acts of eating, breathing, and excreting. Energy exchanges include the absorption and rejection of heat and the performance of mechanical work by body muscles.

In connection with heat flow, we note that extrapolation from experience suggests the idea of a perfect insulator. The technical name for this wondrous device is *adiabatic wall.* A system enclosed by adiabatic walls is unaffected by thermal changes (as opposed to mechancial changes) in its surroundings, and is said to be "thermally isolated." A system is said to be "in thermal contact with its surroundings" whenever its boundaries do not function as adiabatic walls. Two systems in thermal contact are capable of exchanging heat and are often said to be "separated by diathermic or conducting walls."

Students are often disturbed when the concept of an adiabatic wall is thrust upon them, hailed as fundamental, and then used frequently. They are made uneasy by a feeling that thermodynamics is based on a fantasy. How can thermodynamics deal meaningfully with the real world by introducing an abstraction such as the adiabatic wall; that is, something which cannot be "built"? The notion of an adiabatic wall is valid and useful in thermodynamics in precisely the same way that the idea of a frictionless surface is helpful in mechanics: Both can be approached, that is, almost achieved. Mechanical friction cannot be eliminated completely. Nevertheless it is often possible to reduce frictional forces to the point where they are ignorable by comparison with other forces. The lack of complete thermal isolation is likewise often ignorable.

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**1.1.3** Construct a brief list of physical systems, classifying them as open, closed, or isolated. Be prepared to explain your choices of classification, including the extent to which your entries under closed and isolated are approximations.

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## 1.2 STATES—MECHANICAL AND THERMODYNAMIC

Consider a system composed of $N$ particles. The particles might be the atoms comprising your brain or the molecules of the air in some classroom. The mechanical state of the system is fixed by a specification of the position and velocity of each particle. Six variables are required to specify the position and velocity of each particle—three components of the position vector and three components of the velocity vector. Thus, a total of $6N$ microscopic variables is needed to completely specify the mechanical state of an $N$-particle system. If the values of these $6N$ variables are known at some instant, Newton's laws of motion provide a scheme which, in principle only, allows the mechanical state of the system to be determined at any later time.

Statistical physics is concerned with systems for which $N$ is so large that we are unable, as a practical matter, to specify the mechanical state of the system; that is, there are too many microscopic variables of which to keep track.