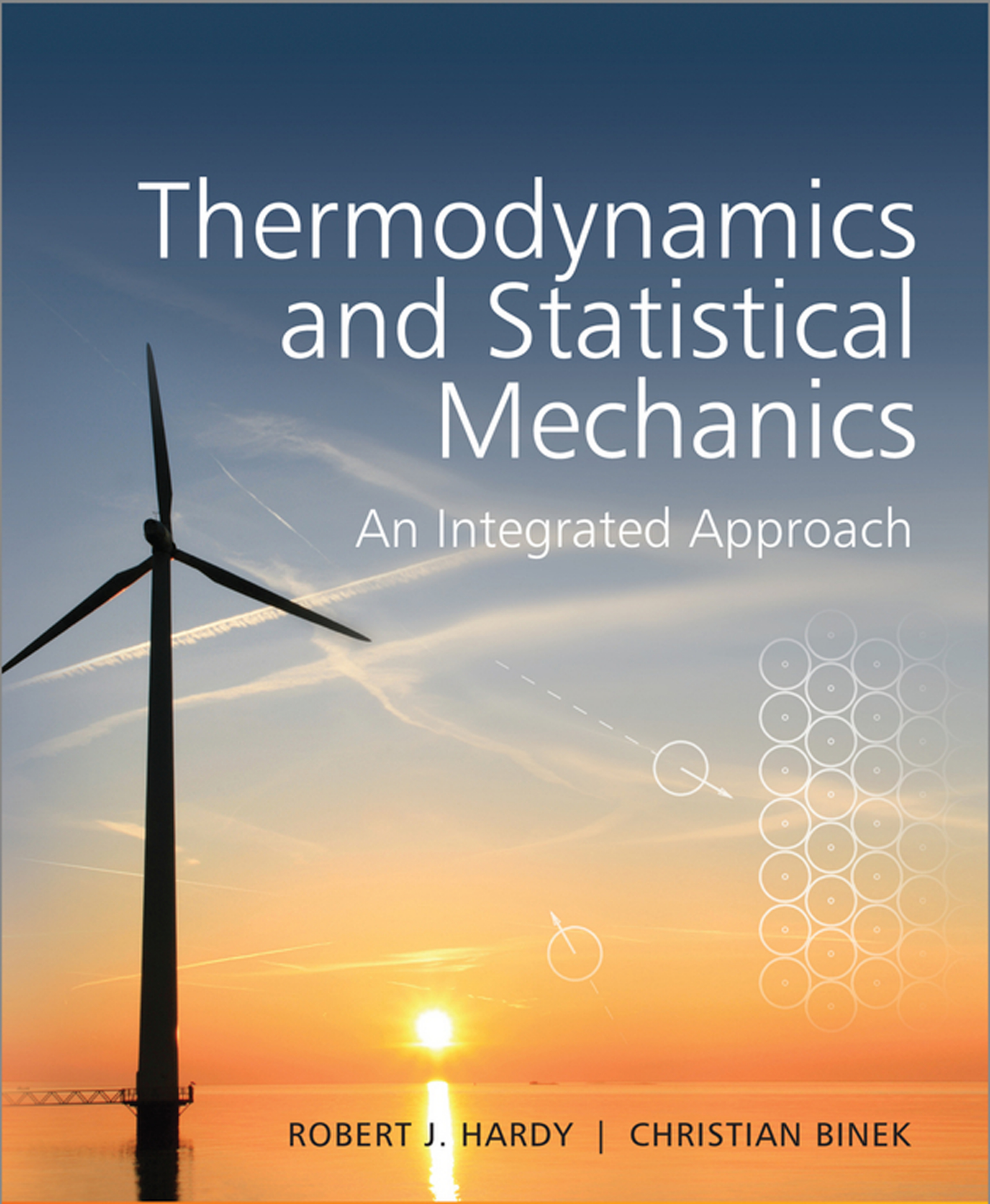

Thermodynamics and Statistical Mechanics

An Integrated Approach

ROBERT J. HARDY | CHRISTIAN BINEK

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ROBERT J. HARDY and CHRISTIAN BINEK
Department of Physics, University of Nebraska-Lincoln, USA

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Preface

This is a text on the fundamentals of thermal physics and includes both the macroscopic and microscopic aspects of the subject. Thermodynamics and statistical mechanics, like classical mechanics, electricity and magnetism, and quantum mechanics, are axiomatic theories based on small numbers of postulates. The two approaches to the subject give very different insights into the nature of thermal phenomena, supply different tools of analysis, and are essential research tools of the practicing physicist. Thermodynamics establishes the basic concepts for describing observed phenomena and establishes general relationships that are exact and independent of assumptions about the structure of matter. Statistical mechanics gives the microscopic basis of thermal behavior and supplies the tools for determining the properties of systems from their atomic level characteristics. The text is ideal for three types of courses: a one-semester course for undergraduates, a two-semester course for advanced undergraduates, and a statistical mechanics course for beginning graduate students. The book is written on the principle that a good text is also a good reference. By combining the macroscopic and microscopic approaches in a single book, we give students studying statistical mechanics a readily available source for reviewing the macroscopic concepts and relationships used in atomic-level studies.

We present thermodynamics and statistical mechanics as self-contained theories. Many texts merge the macroscopic and microscopic approaches and select the approach according to the result being sought. Although practicing scientists often mix concepts from different theories when investigating new situations, is not the best approach when teaching a subject. It leaves students with a hodgepodge of ideas instead of a coherent understanding of fundamentals. Once understood, the fundamentals are available for a wide range of applications.

Our presentation of the macroscopic aspects of the subject is tailored to the backgrounds of modern physics students. The logic of the Clausius–Kelvin formulation of thermodynamics is used, but our presentation is not traditional. We focus on the properties of equilibrium state space and utilize the student's understanding of multidimensional spaces obtained from their studies of mechanics, electricity, and magnetism. The fundamental macroscopic concepts are developed while keeping in mind the student's previous exposure to the atomic-level structure of matter.

Another unique aspect of our book is the treatment of the mathematics involved. We assume that students have completed the standard introductory sequence of calculus courses through partial differentiation and multidimensional integration. Nevertheless, we find that many students, even those who did well in those courses, have difficulties with the mathematics of thermal physics. This is especially true of thermodynamics, partially because they have not seen some of the methods used outside of their mathematics courses and partially because of the notation used. To overcome these difficulties, the essential mathematical concepts are reviewed before using them and the similarity of the mathematics to that employed in the other fields of physics is emphasized.

The book is divided into five parts. Part I introduces the concepts of thermal physics by applications to gases, liquids, and solids while making use of the first law of thermodynamics. Everyday phenomena are used to illustrate the concepts involved. The logical development of thermodynamics is the subject of Part II. The macroscopic concept of entropy is deduced and its importance for addressing concerns about energy conservation is outlined. The thermodynamic potentials are obtained and their role as succinct summaries of the equilibrium properties of systems is described.

Part III acts as a bridge between the macroscopic and microscopic approaches by presenting some intuitive descriptions of the atomic-level origins of thermodynamic behavior. Maxwell's velocity distribution is derived, and Boltzmann's microscopic formula for entropy is introduced.

Statistical mechanics is developed in Parts IV and V and begins with the derivation of the microcanonical, canonical, and grand canonical ensembles. We then develop the general methods for predicting the properties of systems from the microscopic description contained in their Hamiltonians. Starting from the fundamentals, we analyze ideal gases, the Einstein model, harmonic solids, fluctuations, paramagnetism, blackbody radiation, Fermi–Dirac statistics, and Bose–Einstein condensations.

We know from our experience as teachers that a semester is never long enough to present all of the topics we would like to discuss. To facilitate the selection of material, the less essential (but still important) topics are placed toward the ends of chapters. As studying a topic once does not automatically make it part of a student's working knowledge, we make frequent references to results obtained earlier. We are grateful to our students and colleagues for their many suggestions for ways to clarify our presentation of the subject.

We recommend teaching thermodynamics soon after the beginning sequence of courses and before the typical physics curriculum focuses on atomic and subatomic phenomena. A one-semester course for undergraduates can be based on Parts I and II with selections from Part III to introduce the microscopic origins of thermal behavior. The prerequisites for Parts I, II, and III are the standard two- or three-semester sequence of calculus-based physics courses for incoming majors. Since the thermodynamic potentials and the properties of entropy are fundamental to thermodynamics, the course should definitely include the first three sections of both Chapters 11 and 12. However, if time is running short, we recommend skipping the later sections of Part II and going to first chapter of Part III.

Parts IV and V form the core of a one-semester graduate course on statistical mechanics. The prerequisite is an understanding of quantum mechanics through familiarity with the eigenstates of the Schrödinger equation. The first two chapters of Part III should be included as an introduction to the microscopic aspects of statistical physics. Because of the diversity in the undergraduate preparations of beginning graduate students, we recommend beginning with a review of the technical meanings of terms from Chapter 1 and the properties of materials from Chapter 3. Because of their importance of in statistical mechanics, we recommend a brief review the thermodynamic potentials, as presented in the first three sections of Chapter 12. All five parts of the book make an excellent text for a two semester course for advanced undergraduates.

Part I
Elements of Thermal Physics

Thermal physics is concerned with systems that contain large numbers of particles, molecules, atoms, ions, electrons, photons, etc. Thermodynamics describes their *macroscopic* behavior, while the *microscopic* origin of thermal behavior is described by statistical mechanics. Since familiarity with the phenomena involved at the macroscopic level is essential for understanding their microscopic origins, we start with the macroscopic aspects while keeping in mind the atomic-level nature of the systems being studied. Part I introduces the concepts of thermal physics by applications to gases, liquids, and solids, and makes extensive use of the principle of energy conservation as expressed by the first law of thermodynamics. Part II focuses on the second law and the property of entropy.

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Fundamentals

As many of the terms of thermal physics are also used in everyday speech, it is important to understand their more restricted technical meanings. It is especially important to understand the fundamental distinction between heat and work, which describe the interaction of systems with each other, and the intrinsic property of individual systems called internal energy. Other important concepts are equilibrium, state, state function, process, and temperature.

1.1 *PVT* Systems

Pressure P, volume V, and temperature T are essential properties of solids, liquids, and gases. In scientific usage both liquids and gases are fluids, *i.e.*, substances that flow to conform to the shape of their container. Before introducing two relatively simple mathematical models of *PVT* systems, we review the units used in the description of thermodynamic behavior.

Units

The SI units for pressure, volume, and temperature are the pascal (Pa) named after Blaise Pascal, the cubic meter (m^3), and the kelvin (K) named after Lord Kelvin, who is also known as William Thompson. Other commonly used units for volume are the cubic centimeter (cm^3), the liter (L), and the cubic foot (ft^3).

$$1\,\mathrm{m}^3 = 10^3\,\mathrm{L} = 10^6\,\mathrm{cm}^3 = 35.31\,\mathrm{ft}^3. \tag{1.1}$$

One pascal equals one newton per square meter ($1\ \mathrm{Pa} = 1\,\mathrm{N\,m}^{-2}$). In many applications the convenient SI unit for pressure is the kilopascal (kPa). An important reference pressure is the *standard atmosphere* (1 atm), which is approximately 100 kPa.

$$1 \text{ standard atmosphere} = 101.325\,\mathrm{kPa}. \tag{1.2}$$

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Other units for pressure are the bar (1 bar = 100 kPa), the pound per square inch (lb in^{-2}), the millimeter of mercury (mmHg), and the torr (1 torr = 1 mmHg) named after Evangelista Torricelli. The unit “mmHg” is based on the height of the mercury column in a barometer. These units are related by

$$1\,\text{atm} = 101.3\,\text{kPa} = 760\,\text{mmHg} = 760\,\text{torr} = 14.70\,\text{lb in}^{-2}. \tag{1.3}$$

The unit "atm" is sometimes called an atmosphere. The unit specifies a specific force per unit area and must not be confused with the less precise "atmospheric pressure," which is the pressure of the atmosphere and is only *approximately* equal to 1 atm at elevations not too far above sea level.

The commonly used temperature scales are the Kelvin, Celsius, and Fahrenheit scales. The relationship between a Celsius temperature Θ^{C} and a Kelvin temperature T^{K} is

$$\Theta^{\text{C}} = T^{\text{K}} - 273.15. \tag{1.4}$$

The relationship between a Fahrenheit temperature Θ^{F} (in units of °F) and a Celsius temperature Θ^{C} (in units of °C) is

$$\Theta^{\text{F}} = \frac{9}{5}\Theta^{\text{C}} + 32. \tag{1.5}$$

The symbol T is reserved for temperatures measured on an absolute temperature scale, a concept made precise in Chapters 7 and 8. The symbol Θ is used with other temperature scales. The Kelvin scale is an absolute temperature scale. (The symbol for the unit is K, not °K). The Celsius and Fahrenheit scales are not absolute scales. Although the numerical values of temperatures are different in units of K and °C, the values of the *temperature differences* are the same,

$$\Delta T^{\text{K}} = \Delta\Theta^{\text{C}}. \tag{1.6}$$

As indicated in (1.5), a temperature difference of five Celsius degrees is equivalent to a difference of nine Fahrenheit degrees.

Standard temperature and pressure (STP) refers to 273.15 K (0 °C) and 1 standard atmosphere. Room temperature and atmospheric pressure are not precisely defined. This book considers "room temperature" to be 300 K and "atmospheric pressure" to be 100 kPa.

Internal energy U is the thermodynamic property of a system that represents the sum of the kinetic and potential energies of its microscopic constituents. The SI unit for energy is the joule (J) named after James Prescott Joule. In thermal physics the calorie (cal) and kilocalorie (kcal) are convenient units for energy. The food Calorie (written with a capital C) is actually a kilocalorie. The British thermal unit (Btu) is used in engineering. The units of energy are related by

$$4184\,\text{J} = 1\,\text{kcal} = 1000\,\text{cal} = 3.968\,\text{Btu}. \tag{1.7}$$

The internal energy and pressure of *PVT* systems can be expressed as functions of temperature and volume.[1]

$$U = U(T, V) \qquad \text{and} \qquad P = P(T, V). \tag{1.8}$$

---

[1] Equations like $V = V(T, P)$ and $U = U(T, P)$ are *constitutive relations*. The relationship $V = V(T, P)$ is sometimes called the *thermal equation of state* and $U = U(T, P)$ is called the *caloric equation of state*. In this book the phrase "equation of state" is used without modifier and refers to a relationship between P, V, and T.

It is helpful when explaining the concepts of thermodynamics to have explicit expressions for these functions. Ideal gases and simple solids are useful for this purpose.

Ideal Gases

A gas is a collection of molecules that move about in random directions with occasional collisions with each other and with the walls of their container. In many applications real gases are accurately modeled as ideal gases, which are also called *perfect gases*. In the ideal gas model the relationship between pressure, volume, and temperature is

$$PV = nRT. \tag{1.9}$$

where the function $P(T, V)$ is nRT/V. This is the *ideal gas equation of state*, and R is the *universal gas constant*.

$$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} = 1.987\,\mathrm{cal\,mol^{-1}\,K^{-1}} \tag{1.10}$$

and n is the number of moles.

One *mole* is the quantity of material that has a mass in grams equal to its *molecular weight*. The mass m of one molecule of a pure substance is

$$m = (\text{molecular weight}) \cdot m_u = \frac{(\text{molecular weight in grams})}{N_A}, \tag{1.11}$$

where the *atomic mass constant* is

$$m_u = 1.661 \times 10^{-27}\,\mathrm{kg}$$

and the number of molecules per mole is given by *Avogadro's number* named after Amadeo Avogadro.

$$N_A = 6.022 \times 10^{23}\mathrm{mol^{-1}}. \tag{1.12}$$

The internal energy of an ideal gas depends on temperature only, which is a special case of the relationship indicated in (1.8). As there is no dependence on volume, it is expressed by

$$U = U(T). \tag{1.13}$$

It is shown in Chapter 10 that this special case is a consequence of $PV = nRT$. Until then, equations (1.9) and (1.13) are considered the defining characteristics of an ideal gas.

Simple Solids

More than one type of model system is needed to illustrate the generality of thermodynamics. The functions for the internal energy and pressure of another type of system are

$$U = Mc_oT + b_oV\left[\ln\left(\frac{V}{V_o}\right) - 1\right] \tag{1.14}$$

and

$$P = a_oT - b_o\ln\left(\frac{V}{V_o}\right), \tag{1.15}$$

where a_o, b_o, c_o, and V_o are constants and M is the mass of the system. Although less significant that the ideal gas model, the above equations give a useful description of the behavior of solids over the limited ranges of temperatures and pressures of interest in many applications. For this reason a system described by (1.14) and (1.15) will be referred to as a *simple solid*.

It is shown in Chapter 3 that the above equations describe the internal energy and pressure of a system whose coefficient of thermal expansion α_V, bulk modulus B_T, and specific heat c_V^M are constant. Their values for a few solids are given in Table 1.2 on page 15. The equations that relate the a_o, b_o, and c_o to α_V, B_T, and c_V^M are $a_o = \alpha_V B_T$, $b_o = B_T$, and $c_o = c_V^M$ (see (3.28)). The constant V_o is chosen so that (1.15) gives the pressure at some specific temperatures, such as $P = 100\,\text{kPa}$ and $T = 300\,\text{K}$.

The significant differences in the functions for internal energy and pressure for ideal gases and simple solids reflect differences in their microscopic structures. The behavior of solids is dominated by the forces that bind the atoms into a rigid structure. These forces can be obtained from a potential energy function. An approximate expression for the internal energy function is

$$U(T, V) = Mc_oT + \Phi(V). \tag{1.16}$$

The term Mc_oT describes the kinetic and potential energies associated with the vibrational motion of the atoms. The *static energy* $\Phi(V)$ is the energy or the system when the atoms are stationary. The volume of a solid is changed by subjecting it to high pressure. The contribution to pressure resulting from the changes to $\Phi(V)$ is $-d\Phi/dV$. An approximate expression for the pressure is

$$P = a_oT - \frac{d\Phi}{dV}. \tag{1.17}$$

The term a_oT accounts for the tendency of solids to expand as temperature increases. The static energy $\Phi(V)$ is represented in the simple solid model by the term $b_oV[\ln(V/V_o) - 1]$ in (1.14), which implies that $d\Phi/dV = b_o \ln(V/V_o)$. Combining this with (1.17) yields the expression for pressure in (1.15).

1.2 Equilibrium States

System

Many of the systems that will be studied are homogeneous (uniform composition) and isotropic (same in all directions), such as the gas or liquid in a container or a sample of dielectric or magnetic material. Nevertheless, the concepts of thermal physics are applicable to much more complex systems, sometimes referred to as *devices*, such as engines, refrigerators, and electrical generating plants.

A system may be made up of smaller systems, called *subsystems*. We may refer to something as a subsystem at one time and as a system at another time. Sometimes we concentrate on one system and refer to everything it interacts with as its *surroundings*, or the *environment*. Since the focus of a discussion often changes, it is important to clearly identify the system to which the principles of thermodynamics are being applied.

A system with a fixed quantity of matter is a *closed* system, and one that can exchange matter with its surrounding is an *open* system. An automobile engine, which takes in fuel and air and exhausts combustion products, is an open system. The mass of a closed system is constant, and in the absence of chemical reactions the numbers of moles of its different constituents are constant.

Equilibrium

A system is in equilibrium if it does not spontaneously change. A glass of warm water with a cube of ice in it is *not* in equilibrium, as the ice will spontaneously melt until either the water cools to 0.0 °C or all of the ice melts. The tendency of systems to spontaneously change until their temperatures are uniform throughout is a widely observed phenomenon. Systems in *thermal equilibrium* have a uniform temperature.

A system can be in equilibrium even when it is changing, provided the change is caused by a change in the *constraints* on it. Consider the gas confined in a cylinder with a piston at one end, as diagrammed in **Figure 1.1**. The temperature and pressure of the gas will change when the piston is moved. The gas is considered to be in equilibrium as it changes, because it is not changing spontaneously. However, this is only true if the piston is not moved too rapidly. If moved fast enough, the motion will create sound waves that move back and forth within the cylinder, so that the gas will not be in equilibrium until the sound waves die out.

A system may not be changing and yet *not* be in equilibrium. This is the case when its condition is maintained by a continuous exchange of energy with its surroundings. For example, the pane of glass that separates the warm interior of a building from the cold exterior is in a *steady state*, provided the inside and outside temperatures are steady, but the glass is *not* in equilibrium. To maintain the temperature distribution in the glass, heat must be continuously transferred to it from the room and removed by the air outside. If the pane of glass is removed from the wall and isolated, the temperature distribution in it will spontaneously change until it is uniform.

The concept of equilibrium is also important in mechanics. An object is in *mechanical equilibrium* when its translational and rotational velocities do not spontaneously change,

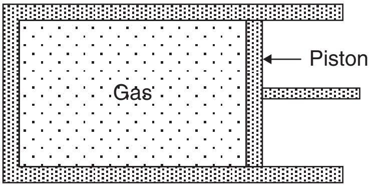

Figure 1.1 *Gas Confined in a Cylinder*

i.e., when its linear acceleration and its angular acceleration are zero. The conditions that must be satisfied for an object to be in mechanical equilibrium are

$$\sum_i \boldsymbol{F}_i = 0 \quad \text{and} \quad \sum_i \boldsymbol{\tau}_i = 0, \tag{1.18}$$

where $\boldsymbol{F}_i$ and $\boldsymbol{\tau}_i$ are the external forces and torques on the object.

State

The concept of state is fundamental but not easy to define. The different *states* of a system refer to different conditions or configurations. For example, a ball could be resting on a table or moving across the room. These mechanical states are described by giving its position, velocity, and angular momentum. The state of a system in quantum mechanics is described by its wave function, which is also called a state function. In thermodynamics we are interested in the *thermodynamic states* of systems, which are also called *equilibrium states*.

The number of properties needed to specify the equilibrium state of a system is the number of *thermodynamic degrees of freedom*. The number depends on the system involved and the type of behavior being investigated. A simple *PVT* system has two degrees of freedom, which can be specified by giving its temperature and volume (T, V) or its temperature and pressure (T, P). Other choices such as internal energy and volume are also used. A homogeneous fluid whose dielectric properties are being investigated has three thermodynamic degrees of freedom: In addition to temperature and pressure, we need to specify the strength of the electric field $\mathcal{E}$.

State Function

Properties whose values are determined by the system's state are called *state functions*. Temperature T, volume V, pressure P, internal energy U, entropy S, enthalpy H, etc. are state functions. When the state of a system is specified by T and V, the values of P, U, S, and H are given by functions $P(T, V)$, $U(T, V)$, $S(T, V)$, and $H(T, V)$. The independent variables T and V are the *thermodynamic coordinates* of the system. The number of thermodynamic coordinates, *i.e.*, the number of independent variables, equals the number of thermodynamic degrees of freedom. State functions are also called state variables. It should be noted that heat Q and work W are *not* state functions. They are process dependent quantities.

State Space

The thermodynamic coordinates that specify a system's state define a space called *thermodynamic state space* or *equilibrium state space*. If no ambiguity results, it is simply called *state space*. As the state space of a homogeneous *PVT* system has two coordinates, we can represent its states by points on a two dimensional graph. More coordinates are required for more complex systems. For example, in a system of ice and water, a third coordinate is required to specify the fraction of the system that is ice (or water).

Internal Energy

When viewed microscopically, thermodynamic systems are collections of electrons, atoms, and molecules. The energy associated with these microscopic constituents is determined by the velocities and positions of the huge number of constituent particles, which is typically of the order of Avogadro's number. In contrast, when in thermal equilibrium, the system's internal energy is determined by its thermodynamic coordinates which are few in number. The existence of the internal energy state function is fundamental to thermodynamics.

Equation of State

The relationship between pressure, volume, and temperature in a *PVT* system is called the *equation of state* and can be expressed as $P = P(T, V)$, $V = V(T, P)$, or $T = T(P, V)$. A general form that treats the properties symmetrically is

$$F(P, V, T) = 0. \tag{1.19}$$

For ideal gases the explicit expressions for the functions $P(T, V)$, $V(T, P)$, and $T(P, V)$ are nRT/V, nRT/P, PV/nR, and PV/nR, respectively. The expression for $F(P, V, T)$ is $(PV - nRT)$, and the equation of state is usually written as $(PV = nRT)$.

Example 1.1 $V(T, P)$ and $U(T, P)$ for simple solids

Find the functions that give the dependence of the volume and internal energy of a simple solid on its temperature and pressure.

Solution. According to (1.14) and (1.15), the functions for the pressure and internal energy of a simple solid are

$$P(T, V) = a_o T - b_o \ln(V/V_o)$$

and

$$U(T, V) = M c_o T + b_o V[\ln(V/V_o) - 1].$$

To find the dependence V and U on the system's state when the thermodynamic coordinates are (T, P), instead of (T, V), we rewrite the above expression for pressure as $\ln(V/V_o) = (a_o T - P)/b_o$. It then follows that the function for the dependence of volume on temperature and pressure is

$$V(T, P) = V_o e^{(a_o T - P)/b_o}. \tag{1.20}$$

The function that gives the dependence of the internal energy on temperature and pressure is $U(T, P) = U(T, V(T, P))$. Substituting the expression for $V(T, P)$ into the expression for $U(T, V)$ gives

$$U(T, P) = M c_o T + (a_o T - P - b_o) V_o e^{(a_o T - P)/b_o}. \tag{1.21}$$

The significant difference in the appearance of the expressions for $U(T, V)$ and $U(T, P)$ illustrates the extent to which the functional form of state functions depend on the choice of thermodynamic coordinates.

1.3 Processes and Heat

A process starts at an initial time t_0 and ends at some final time t_f ($t_0 < t_f$) and brings about a change in the state of the system. Thermodynamics is concerned with the direction in which processes evolve but not in its rate of evolution. Although the system is often not in equilibrium at all times throughout a process, it is usually assumed to be in thermal equilibrium at the start and end.

Equilibrium and Quasi-Static Processes

A process in which the system is in equilibrium at all times between time t_0 and time t_f is an *equilibrium process*. If at any time during the process the system is not in equilibrium, it is a *nonequilibrium process*. In equilibrium processes, a system changes in response to changes in the constraints and stops changing when the constraints stop changing. Many processes can be idealized as equilibrium processes, provided they proceed sufficiently slowly, where the meaning of slowly depends on the process. For example, the compression of the air-fuel mixture in the cylinders of an automobile engine, which occurs in a time of the order of a hundredth of a second, is often idealized as an equilibrium process. In contrast, the melting of an ice cube placed in a glass of water, which may take several minutes, is not an equilibrium process.

Equilibrium processes are sometimes called quasi-static processes. A *quasi-static* (almost-unchanging) process is one that is performed slowly enough that the system is effectively in equilibrium at all times. The term "equilibrium process" is preferred to "quasi-static process," because it suggests the useful characteristic of being representable by a line in state space.

As the state space of a *PVT* system is two dimensional, an equilibrium process can be represented by a line on a two dimensional graph. When the thermodynamic coordinates are pressure and volume, the graph is called a *PV*-diagram. Some important equilibrium processes in ideal gases are shown in **Figure 1.2**. The point "0" represents the initial state of the gas. The points labeled "*f*" represent the final states. An *isothermal process* is a

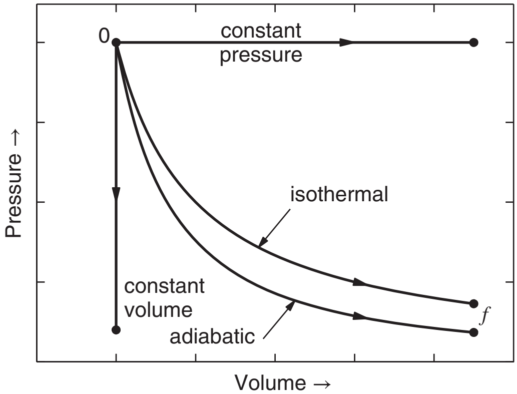

Figure 1.2 *PV-Diagram of Equilibrium Processes*

constant-temperature process, and a line at constant temperature is an *isotherm*. An *isobaric process* is a constant-pressure process, and a line at constant pressure is an *isobar*. A constant-volume process in a *PVT* system is sometimes called an *isochoric process*, which indicates that no work is done. Adiabatic processes are discussed below. As the points on lines represent equilibrium states, nonequilibrium processes are not representable by lines in state space.

Reversible Processes

A *reversible process* is one whose direction in time can be reversed. A process that starts in state "0" and proceeds along a line in state space to state "*f*" is reversed by starting in state "*f*" and traversing the same line in the opposite direction. Processes that can be idealized as reversible are especially important in thermodynamics. In practice, a reversible process is made to evolve in the reversed direction by a small change in the constraints on the system. Although equilibrium, quasi-static, and reversible processes have different defining characteristics, processes with the characteristics of one type also have the characteristics of the other types.

Heat

The word "heat" is familiar to us from everyday life. Although its technical meaning is consistent with colloquial usage, it is much more restricted. Unlike temperature and internal energy, heat does not describe the condition of a system, but instead describes what is happening during a process. The heat transferred to a system is represented by Q. By convention, Q is positive when the energy is transferred *to* the system and negative when energy is transferred *from* it. The heat transferred *to* one system *from* another is the negative of the heat transferred *to* the second system *from* the first.

We can increase the temperature of water by putting it in a container over a flame or on a hot plate. We can cool a hot object by putting it in cold water. When doing these things, something appears to pass between the water and its surroundings. That something is heat: *Heat is the energy transferred from one system to another because of a temperature difference*.

Adiabatic Processes

Adiabatic processes are important both in applications and in establishing the foundations of thermodynamics. *An adiabatic process is one in which no heat is accepted or rejected by the system at any time during the process*. An *adiabatically isolated* system is one that cannot exchange heat with its surroundings. In everyday speech we would say the system is perfectly insulated. The contents of a high quality Dewar flask, named after its inventor Sir James Dewar, is an example of an adiabatically isolated system. Dewar flasks are double-walled containers with the space between the walls evacuated to prevent the transfer of heat by conduction, and the inside surfaces of the walls are silvered to minimize heat transfer by radiation.

Adiabatic processes can be either reversible or irreversible. When a gas is compressed with no exchange of heat with its container, the process in the gas is both reversible and adiabatic. In contrast, when some ice is added to the hot water in a Dewar flask, the process in the contents of the flask is adiabatic but *not* reversible. Interfaces across which heat *cannot* be exchanged are *adiabatic boundaries*. Interfaces across which heat *can* be exchanged are sometimes called *diathermic boundaries*.

1.4 Temperature

Thermally Interacting Systems

Systems that can exchange heat with each other are in *thermal contact*, and a system with no adiabatically isolated parts is a *thermally interacting system*. When in thermal equilibrium, a thermally interacting system possesses a single temperature. In contrast, systems made up of two or more adiabatically isolated subsystems can have more than one temperature. For example, the contents of a Dewar flask and the space outside can be thought of as a single system. Although the system may be in equilibrium, *i.e.*, not spontaneously changing, it will possesses two temperatures, *i.e.* the temperature of the contents and the temperature of the space outside.

Temperature

The concepts of heat and temperature are closely related. Temperature is a state function that describes the tendency of a system (or subsystem) to exchange heat with other systems: (i) All systems in thermal contact have the same temperature when in thermal equilibrium and no heat is exchanged between them. (ii) Systems with different initial temperatures spontaneously exchange heat when brought into thermal contact. The direction of the exchange is described by saying that heat is transferred from the *hotter* system to the *colder* system. On the Kelvin, Celsius, and Fahrenheit temperature scales the hotter system has the higher temperature. The data in Table 1.1 illustrates the wide range of temperatures possessed by various systems.

Thermometers

A thermometer is a device that possesses an equilibrium property that is easily observed and depends on the tendency of the device to exchange heat. The significant property of a

Table 1.1 *Miscellaneous temperatures*

1.5×10^7 K	Estimated temperature at the center of sun
5800 K	Approximate temperature of the surface of sun
1809 K	Iron melts (1536 °C)
273.15 K	Ice point (0 °C)
234 K	Mercury freezes (−39 °C)
195 K	Solid carbon dioxide (dry ice) sublimes at 1 atm (−78 °C)
77 K	Nitrogen liquefies at 1 atm (−196 °C)
4.2 K	Helium liquefies at 1 atm
10^{-8} K	Bose–Einstein condensation of Rb gas (first observed in 1996)

liquid-in-glass thermometer is the length of the column of liquid. The significant property in many laboratory thermometers is an electrical resistance or a voltage. To measure the temperature of a system, we bring it into thermal contact with the thermometer and let the combined system come into thermal equilibrium. As the system and thermometer have the same temperature, the system is assigned the temperature of the thermometer.

Local Temperature

We sometimes need to distinguish between the fundamental concept of temperature and the reading on a thermometer. The distinction is made by calling the equilibrium state function an *equilibrium temperature* and the reading on a thermometer a *local temperature*. Systems that are not in equilibrium do not have an equilibrium temperature but may have local temperatures, which in general are different at different locations. The local temperature at a particular location is the temperature a thermometer would indicate if placed in thermal contact at that point. A system in thermal equilibrium has the same local temperature throughout, and its value is the same as the equilibrium temperature. When a system is rapidly changing, very small, or far from equilibrium, it may not be possible to assign values to the local temperature.

Zeroth Law

Two systems in thermal equilibrium with a third will be in thermal equilibrium with each other when brought into contact. This statement is often called the *zeroth law of thermodynamics*. Essentially, it is an assertion that the concept of thermal equilibrium is transitive. Transitive relationships are important in science, but are usually not called laws. For example, an equal arm balance can be used to compare the weights of objects, but it is assumed without calling it a law that two objects that individually balance a third can balance each other. As its unusual numbering suggests, the zeroth law does not have the significance of the first and second laws of thermodynamics.

Heat Reservoirs

A heat reservoir is an idealization of a system that can transfer significant amounts of heat to or from a system with no change in its temperature. It is a source or sink of heat with a fixed tendency to exchange heat. They are also called *heat baths*. For example, to maintain an object at a constant temperature of 0 °C, we can use a mixture of ice and water as a heat reservoir.

1.5 Size Dependence

Intensive Versus Extensive

Thermodynamic properties can be either intensive or extensive. *Intensive properties are independent of the size of the system. Extensive properties are proportional to size*. Temperature T and pressure P are intensive, while mass M, number of moles n, volume V, and internal energy U are extensive. *Extensive properties are additive*. For example, the values of the mass, volume, and internal energy of systems consisting of several subsystems are the sums of the masses, volumes, and internal energies of the subsystems.

When a system is made up of N identical subsystems, the values of its extensive variables (properties) are N times their values in the subsystems, while the values of its intensive variables are the same as the values in the subsystems. The sizes of homogeneous systems can be varied continuously. *When the size of a homogeneous system is scaled by a factor of* λ, *the values of its extensive properties are multiplied by* λ, *while its intensive properties remain unchanged*. For example, if a system whose mass, volume, internal energy, temperature, and pressure are M_0, V_0, U_0, T_0, and P_0 has its size increased by 20%, so that $\lambda = 1.20$, its mass, volume, and internal energy will become $M = 1.2M_0$, $V = 1.2\,V_0$, and $U = 1.2\,U_0$, while its temperature and pressure remain unchanged.

Intensive variables can be formed by dividing one extensive variable by another. For example,

$$\rho = \frac{M}{V}, \tag{1.22}$$

where the *mass density* ρ is intensive while mass M and volume V are extensive. An intensive property, obtained by dividing by the mass M or the number of moles n, is called a *specific* property. For example, depending on the divisor, the *specific volume* of a system is

$$v_M = \frac{V}{M} \quad \text{or} \quad v = \frac{V}{n}. \tag{1.23}$$

The subscript on v_M identifies it as a "per unit mass" property. A "per mole" value is also called a molar value. When expressed in terms of the specific volume V/n, the ideal gas equation of state simplifies to

$$Pv = RT. \tag{1.24}$$

When an extensive property is represented by a capital letter, it is convenient (but not always practical) to represent the associated intensive property by the same letter in lower case. The characteristics of the material that makes up a homogeneous system are specific values that can be listed in tables of material properties, like those in Table 1.2. The intensive property M/n obtained by dividing the mass of a pure substance in grams by the number of moles is the *molecular weight* of the substance.

In beginning physics courses, we learn that terms that are added or subtracted in an equation must all have the same units. Similarly, terms with thermodynamic significance that are added or subtracted in an equation must have the same size dependence, *i.e.*, the same intensive or extensive character. Also, except for functions that are powers, such as $f(x) = cx^n$, the arguments of the functions used should be dimensionless and intensive. Logarithms are a special case.

1.6 Heat Capacity and Specific Heat

Heat capacities describe the change in the temperature of a system that results from a transfer of heat. More heat is required to raise the temperature by (say) 10° when the system is a kilogram of water than when it is a kilogram of aluminum. Heat capacities are found by measuring an initial temperature T_0, transferring a small amount of heat Q to a system, and