

## INTRODUCTION

### The Nature of Thermodynamics and the Basis of ThermoStatistics

Whether we are physicists, chemists, biologists, or engineers, our primary interface with nature is through the properties of macroscopic matter. Those properties are subject to universal regularities and to stringent limitations. Subtle relationships exist among apparently unconnected properties.

The existence of such an underlying order has far reaching implications. Physicists and chemists familiar with that order need not confront each new material as a virgin puzzle. Engineers are able to anticipate limitations to device designs predicated on creatively imagined (but yet undiscovered) materials with the requisite properties. And the specific form of the underlying order provides incisive clues to the structure of fundamental physical theory.

Certain primal concepts of thermodynamics are intuitively familiar. A metallic block released from rest near the rim of a smoothly polished metallic bowl oscillates within the bowl, approximately conserving the sum of potential and kinetic energies. But the block eventually comes to rest at the bottom of the bowl. Although the mechanical energy appears to have vanished, an observable effect is wrought upon the material of the bowl and block; they are very slightly, but perceptibly, "warmer." Even before studying thermodynamics, we are qualitatively aware that the mechanical energy has merely been converted to another form, that the fundamental principle of energy conservation is preserved, and that the physiological sensation of "warmth" is associated with the thermodynamic concept of "temperature."

Vague and undefined as these observations may be, they nevertheless reveal a notable dissimilarity between thermodynamics and the other branches of classical science. Two prototypes of the classical scientific paradigm are mechanics and electromagnetic theory. The former addresses itself to the dynamics of particles acted upon by forces, the latter to the dynamics of the fields that mediate those forces. In each of these cases a new "law" is formulated—for mechanics it is Newton's Law (or Lagrange or Hamilton's more sophisticated variants); for electromagnetism it is the Maxwell equations. In either case it remains only to explicate the consequences of the law.

Thermodynamics is quite different. It neither claims a unique domain of systems over which it asserts primacy, nor does it introduce a new fundamental law analogous to Newton's or Maxwell's equations. In contrast to the specificity of mechanics and electromagnetism, the hallmark of thermodynamics is generality. Generality first in the sense that thermodynamics applies to all types of systems in macroscopic aggrega-

tion, and second in the sense that thermodynamics does not predict specific numerical values for observable quantities. Instead, thermodynamics sets limits (*inequalities*) on permissible physical processes, and it establishes relationships among apparently unrelated properties.

The contrast between thermodynamics and its counterpart sciences raises fundamental questions which we shall address directly only in the final chapter. There we shall see that whereas thermodynamics is not based on a new and particular law of nature, it instead reflects a commonality or universal feature of *all* laws. In brief, *thermodynamics is the study of the restrictions on the possible properties of matter that follow from the symmetry properties of the fundamental laws of physics.*

The connection between the symmetry of fundamental laws and the macroscopic properties of matter is not trivially evident, and we do not attempt to derive the latter from the former. Instead we follow the postulatory formulation of thermodynamics developed in the first edition of this text, returning to an interpretive discussion of symmetry origins in Chapter 21. But even the preliminary assertion of this basis of thermodynamics may help to prepare the reader for the somewhat uncommon form of thermodynamic theory. Thermodynamics inherits its universality, its nonmetric nature, and its emphasis on relationships from its symmetry parentage.

# 1

## THE PROBLEM AND THE POSTULATES

### 1-1 THE TEMPORAL NATURE OF MACROSCOPIC MEASUREMENTS

Perhaps the most striking feature of macroscopic matter is the incredible simplicity with which it can be characterized. We go to a pharmacy and request one liter of ethyl alcohol, and that meager specification is pragmatically sufficient. Yet from the atomistic point of view, we have specified remarkably little. A complete mathematical characterization of the system would entail the specification of coordinates and momenta for each molecule in the sample, plus sundry additional variables descriptive of the internal state of each molecule—altogether at least  $10^{23}$  numbers to describe the liter of alcohol! A computer printing one coordinate each microsecond would require 10 billion years—the age of the universe—to list the atomic coordinates. Somehow, among the  $10^{23}$  atomic coordinates, or linear combinations of them, all but a few are macroscopically irrelevant. The pertinent few emerge as *macroscopic coordinates*, or “thermodynamic coordinates.”

Like all sciences, thermodynamics is a description of the results to be obtained in particular types of measurements. The character of the contemplated measurements dictates the appropriate descriptive variables; these variables, in turn, ordain the scope and structure of thermodynamic theory.

The key to the simplicity of macroscopic description, and the criterion for the choice of thermodynamic coordinates, lies in two attributes of macroscopic measurement. *Macroscopic measurements are extremely slow on the atomic scale of time, and they are extremely coarse on the atomic scale of distance.*

While a macroscopic measurement is being made, the atoms of a system go through extremely rapid and complex motions. To measure the length of a bar of metal we might choose to calibrate it in terms of the wavelength of yellow light, devising some arrangement whereby reflection

from the end of the bar produces interference fringes. These fringes are then to be photographed and counted. The duration of the measurement is determined by the shutter speed of the camera—typically on the order of one hundredth of a second. But the characteristic period of vibration of the atoms at the end of the bar is on the order of  $10^{-15}$  seconds!

A macroscopic observation cannot respond to those myriads of atomic coordinates which vary in time with typical atomic periods. *Only those few particular combinations of atomic coordinates that are essentially time independent are macroscopically observable.*

The word *essentially* is an important qualification. In fact we are able to observe macroscopic processes that are almost, but not quite, time independent. With modest difficulty we might observe processes with time scales on the order of  $10^{-7}$  s or less. Such observable processes are still enormously slow relative to the atomic scale of  $10^{-15}$  s. It is rational then to first consider the *limiting* case and to erect a theory of time-independent phenomena. Such a theory is thermodynamics.

*By definition, suggested by the nature of macroscopic observations, thermodynamics describes only static states of macroscopic systems.*

Of all the  $10^{23}$  atomic coordinates, or combinations thereof, only a few are time independent.

Quantities subject to conservation principles are the most obvious candidates as time-independent thermodynamic coordinates: the energy, each component of the total momentum, and each component of the total angular momentum of the system. But there are other time-independent thermodynamic coordinates, which we shall enumerate after exploring the *spatial* nature of macroscopic measurement.

## 1-2 THE SPATIAL NATURE OF MACROSCOPIC MEASUREMENTS

Macroscopic measurements are not only extremely slow on the atomic scale of time, but they are correspondingly coarse on the atomic scale of distance. We probe our system always with "blunt instruments." Thus an optical observation has a resolving power defined by the wavelength of light, which is on the order of 1000 interatomic distances. The smallest resolvable volume contains approximately  $10^9$  atoms! *Macroscopic observations sense only coarse spatial averages of atomic coordinates.*

The two types of averaging implicit in macroscopic observations together effect the enormous reduction in the number of pertinent variables, from the initial  $10^{23}$  atomic coordinates to the remarkably small number of thermodynamic coordinates. The manner of reduction can be illustrated schematically by considering a simple model system, as shown in Fig. 1.1. The model system consists not of  $10^{23}$  atoms, but of only 9. These atoms are spaced along a one-dimensional line, are constrained to

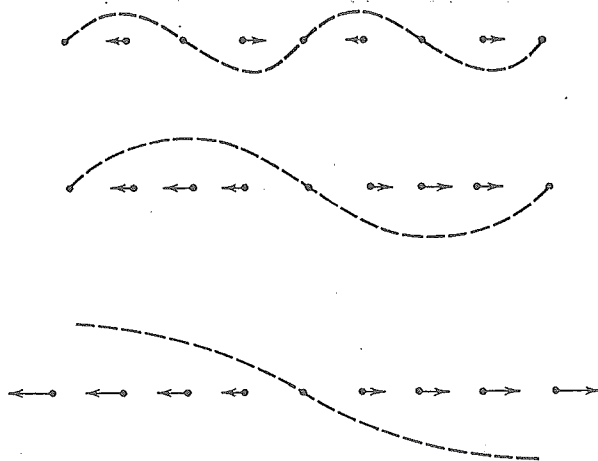


FIGURE 1.1

Three normal modes of oscillation in a nine-atom model system. The wave lengths of the three modes are four, eight and sixteen interatomic distances. The dotted curves are a transverse representation of the longitudinal displacements.

move only along that line, and interact by linear forces (as if connected by springs).

The motions of the individual atoms are strongly coupled, so the atoms tend to move in organized patterns called *normal modes*. Three such normal modes of motion are indicated schematically in Fig. 1.1. The arrows indicate the displacements of the atoms at a particular moment; the atoms oscillate back and forth, and half a cycle later all the arrows would be reversed.

Rather than describe the atomic state of the system by specifying the position of each atom, it is more convenient (and mathematically equivalent) to specify the instantaneous amplitude of each normal mode. These amplitudes are called *normal coordinates*, and the number of normal coordinates is exactly equal to the number of atomic coordinates.

In a "macroscopic" system composed of only nine atoms there is no precise distinction between "macroscopic" and "atomic" observations. For the purpose of illustration, however, we think of a macroscopic observation as a kind of "blurred" observation with low resolving power; the spatial coarseness of macroscopic measurements is qualitatively analogous to visual observation of the system through spectacles that are somewhat out of focus. Under such observation the fine structure of the first two modes in Fig. 1.1 is unresolvable, and these modes are rendered unobservable and macroscopically irrelevant. The third mode, however, corresponds to a relatively *homogeneous net expansion* (or contraction) of the whole system. Unlike the first two modes, it is easily observable through "blurring spectacles." The amplitude of this mode describes the length (or volume, in three dimensions) of the system. *The length (or*

*volume*) remains as a thermodynamic variable, undestroyed by the spatial averaging, because of its spatially homogeneous (long wavelength) structure.

The time averaging associated with macroscopic measurements augments these considerations. Each of the normal modes of the system has a characteristic frequency, the frequency being smaller for modes of longer wavelength. The frequency of the third normal mode in Fig. 1.1 is the lowest of those shown, and if we were to consider systems with very large numbers of atoms, the frequency of the longest wavelength mode would approach zero (for reasons to be explored more fully in Chapter 21). Thus all the short wavelength modes are lost in the time averaging, but *the long wavelength mode corresponding to the "volume" is so slow that it survives the time averaging as well as the spatial averaging.*

This simple example illustrates a very general result. Of the enormous number of atomic coordinates, a very few, with unique symmetry properties, survive the statistical averaging associated with a transition to a macroscopic description. Certain of these surviving coordinates are mechanical in nature—they are volume, parameters descriptive of the shape (components of elastic strain), and the like. Other surviving coordinates are electrical in nature—they are electric dipole moments, magnetic dipole moments, various multipole moments, and the like. *The study of mechanics (including elasticity) is the study of one set of surviving coordinates. The subject of electricity (including electrostatics, magnetostatics, and ferromagnetism) is the study of another set of surviving coordinates.*

*Thermodynamics, in contrast, is concerned with the macroscopic consequences of the myriads of atomic coordinates that, by virtue of the coarseness of macroscopic observations, do not appear explicitly in a macroscopic description of a system.*

Among the many consequences of the "hidden" atomic modes of motion, the most evident is the ability of these modes to act as a repository for energy. Energy transferred via a "mechanical mode" (i.e., one associated with a mechanical macroscopic coordinate) is called *mechanical work*. Energy transferred via an "electrical mode" is called *electrical work*. Mechanical work is typified by the term  $-P dV$  ( $P$  is pressure,  $V$  is volume), and electrical work is typified by the term  $-E_e d\mathcal{P}$  ( $E_e$  is electric field,  $\mathcal{P}$  is electric dipole moment). These energy terms and various other mechanical and electrical work terms are treated fully in the standard mechanics and electricity references. *But it is equally possible to transfer energy via the hidden atomic modes of motion as well as via those that happen to be macroscopically observable.* An energy transfer via the hidden atomic modes is called *heat*. Of course this descriptive characterization of heat is not a sufficient basis for the formal development of thermodynamics, and we shall soon formulate an appropriate operational definition.

With this contextual perspective we proceed to certain definitions and conventions needed for the theoretical development.

### 1-3 THE COMPOSITION OF THERMODYNAMIC SYSTEMS

Thermodynamics is a subject of great generality, applicable to systems of elaborate structure with all manner of complex mechanical, electrical, and thermal properties. We wish to focus our chief attention on the thermal properties. Therefore it is convenient to idealize and simplify the mechanical and electrical properties of the systems that we shall study initially. Similarly, in mechanics we consider uncharged and unpolarized systems; whereas in electricity we consider systems with no elastic compressibility or other mechanical attributes. The generality of either subject is not essentially reduced by this idealization, and after the separate content of each subject has been studied it is a simple matter to combine the theories to treat systems of simultaneously complicated electrical and mechanical properties. Similarly, in our study of thermodynamics we idealize our systems so that their mechanical and electrical properties are almost trivially simple. When the essential content of thermodynamics has thus been developed, it again is a simple matter to extend the analysis to systems with relatively complex mechanical and electrical structure. The essential point to be stressed is that the restrictions on the types of systems considered in the following several chapters are *not* basic limitations on the generality of thermodynamic theory but are adopted merely for simplicity of exposition.

We (temporarily) restrict our attention to *simple systems*, defined as *systems that are macroscopically homogeneous, isotropic, and uncharged, that are large enough so that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields.*

For such a simple system there are no macroscopic electric coordinates whatsoever. The system is uncharged and has neither electric nor magnetic dipole, quadrupole, or higher-order moments. All elastic shear components and other such mechanical parameters are zero. The volume  $V$  does remain as a relevant mechanical parameter. Furthermore, a simple system has a definite *chemical composition* which must be described by an appropriate set of parameters. One reasonable set of composition parameters is the numbers of molecules in each of the chemically pure components of which the system is a mixture. Alternatively, to obtain numbers of more convenient size, we adopt the *mole numbers*, defined as the actual number of each type of molecule divided by Avogadro's number ( $N_A = 6.02217 \times 10^{23}$ ).

This definition of the mole number refers explicitly to the "number of molecules," and it therefore lies outside the boundary of purely macroscopic physics. An equivalent definition which avoids the reference to molecules simply designates 12 grams as the molar mass of the isotope  $^{12}\text{C}$ . The molar masses of other isotopes are then defined to stand in the same ratio as the conventional "atomic masses," a partial list of which is given in Table 1.1.

TABLE 1.1  
Atomic Masses (g) of Some Naturally  
Occurring Elements (Mixtures of Isotopes)<sup>a</sup>

H	1.0080	F	18.9984
Li	6.941	Na	22.9898
C	12.011	Al	26.9815
N	14.0067	S	32.06
O	15.9994	Cl	35.453

<sup>a</sup> As adopted by the International Union of Pure and Applied Chemistry, 1969.

If a system is a mixture of  $r$  chemical components, the  $r$  ratios  $N_k/(\sum_{j=1}^r N_j)$  ( $k = 1, 2, \dots, r$ ) are called the *mole fractions*. The sum of all  $r$  mole fractions is unity. The quantity  $V/(\sum_{j=1}^r N_j)$  is called the *molar volume*.

The macroscopic parameters  $V, N_1, N_2, \dots, N_r$  have a common property that will prove to be quite significant. Suppose that we are given two identical systems and that we now regard these two systems taken together as a single system. The value of the volume for the composite system is then just twice the value of the volume for a single subsystem. Similarly, each of the mole numbers of the composite system is twice that for a single subsystem. Parameters that have values in a composite system equal to the sum of the values in each of the subsystems are called *extensive parameters*. Extensive parameters play a key role throughout thermodynamic theory.