# CHAPTER 1

## INTRODUCTION

### 1.1 What is thermodynamics?

Thermodynamics is the science which has evolved from the original investigations in the 19th century into the nature of "heat." At the time, the leading theory of heat was that it was a type of fluid, which could flow from a hot body to a colder one when they were brought into contact. We now know that what was then called "heat" is not a fluid, but is actually a form of energy – it is the energy associated with the continual, random motion of the atoms which compose macroscopic matter, which we can't see directly.

This type of energy, which we will call *thermal energy*, can be converted (at least in part) to other forms which we *can* perceive directly (for example, kinetic, gravitational, or electrical energy), and which can be used to do useful things such as propel an automobile or a 747. The principles of thermodynamics govern the conversion of thermal energy to other, more useful forms.

For example, an automobile engine can be though of as a device which first converts chemical energy stored in fuel and oxygen molecules into thermal energy by combustion, and then extracts part of that thermal energy to perform the work necessary to propel the car forward, overcoming friction. Thermodynamics is critical to all steps in this process (including determining the level of pollutants emitted), and a careful thermodynamic analysis is required for the design of fuel-efficient, low-polluting automobile engines. In general, thermodynamics plays a vital role in the design of any engine or power-generating plant, and therefore a good grounding in thermodynamics is required for much work in engineering.

If thermodynamics only governed the behavior of engines, it would probably be the most economically important of all sciences, but it is much more than that. Since the chemical and physical state of matter depends strongly on how much thermal energy it contains, thermodynamic principles play a central role in any description of the properties of matter. For example, thermodynamics allows us to understand why matter appears in different phases (solid, liquid, or gaseous), and under what conditions one phase will transform to another. The composition of a chemically-reacting mixture which is given enough time to come to "equilibrium" is also fully determined by thermodynamic principles (even though thermodynamics alone can't tell us how fast it will get there). For these reasons, thermodynamics lies at the heart of materials science, chemistry, and biology.

Thermodynamics in its original form (now known as *classical* thermodynamics) is a theory which is based on a set of postulates about how macroscopic matter behaves. This theory was developed in the 19th century, before the atomic nature of matter was accepted, and it makes no reference to atoms. The postulates (the most important of which are energy conservation and the impossibility of complete conversion of heat to useful work) can't be derived within the context of classical, macroscopic physics, but if one accepts them, a very powerful theory results, with predictions fully in agreement with experiment.

When at the end of the 19th century it finally became clear that matter was composed of atoms, the physicist Ludwig Boltzmann showed that the postulates of classical thermodynamics emerged naturally from consideration of the microscopic atomic motion. The key was to give up trying to track the atoms individually and instead take a statistical, probabilistic approach, averaging over the behavior of a large number of atoms. Thus, the very successful postulates of classical thermodynamics were given a firm physical foundation. The science of *statistical mechanics* begun by Boltzmann encompasses everything in classical thermodynamics, but can do more also. When combined with quantum mechanics in the 20th century, it became possible to explain essentially all observed properties of macroscopic matter in terms of atomic-level physics, including esoteric states of matter found in neutron stars, superfluids, superconductors, etc. Statistical physics is also currently making important contributions in biology, for example helping to unravel some of the complexities of how proteins fold.

Even though statistical mechanics (or statistical thermodynamics) is in a sense "more fundamental" than classical thermodynamics, to analyze practical problems we usually take the macroscopic approach. For example, to carry out a thermodynamic analysis of an aircraft engine, its more convenient to think of the gas passing through the engine as a continuum fluid with some specified properties rather than to consider it to be a collection of molecules. But we do use statistical thermodynamics even here to calculate what the appropriate property values (such as the heat capacity) of the gas should be.

## 1.2 Energy and Entropy

The two central concepts of thermodynamics are *energy* and *entropy*. Most other concepts we use in thermodynamics, for example temperature and pressure, may actually be defined in terms of energy and entropy. Both energy and entropy are properties of physical systems, but they have very different characteristics. Energy is conserved: it can neither be produced nor destroyed, although it is possible to change its form or move it around. Entropy has a different character: it can't be destroyed, but it's easy to produce more entropy (and almost everything that happens actually does). Like energy, entropy too can appear in different forms and be moved around.

A clear understanding of these two properties and the transformations they undergo in physical processes is the key to mastering thermodynamics and learning to use it confidently to solve practical problems. Much of this book is focused on developing a clear picture of energy and entropy, explaining their origins in the microscopic behavior of matter, and developing effective methods to analyze complicated practical processes<sup>1</sup> by carefully tracking what happens to energy and entropy.

# 1.3 Some Terminology

Most fields have their own specialized terminology, and thermodynamics is certainly no exception. A few important terms are introduced here, so we can begin using them in the next chapter.

#### 1.3.1 System and Environment

In thermodynamics, like in most other areas of physics, we focus attention on only a small part of the world at a time. We call whatever object(s) or region(s) of space we are studying the *system*. Everything else surrounding the system (in principle including the entire universe) is the *environment*. The boundary between the system and the environment is, logically, the *system boundary*. The starting point of any thermodynamic analysis is a careful definition of the system.



 $<sup>^{1}</sup>$ Rocket motors, chemical plants, heat pumps, power plants, fuel cells, aircraft engines, . . .



Figure 1.1: Control masses and control volumes.

#### 1.3.2 Open, closed, and isolated systems

Any system can be classified as one of three types: open, closed, or isolated. They are defined as follows:

- **open system:** Both energy and matter can be exchanged with the environment. Example: an open cup of coffee.
- **closed system:** energy, but not matter, can be exchanged with the environment. Examples: a tightly capped cup of coffee.
- isolated system: Neither energy nor matter can be exchanged with the environment in fact, no interactions with the environment are possible at all. Example (approximate): coffee in a closed, well-insulated thermos bottle.

Note that no system can truly be isolated from the environment, since no thermal insulation is perfect and there are always physical phenomena which can't be perfectly excluded (gravitational fields, cosmic rays, neutrinos, etc.). But good approximations of isolated systems can be constructed. In any case, isolated systems are a useful conceptual device, since the energy and mass contained inside them stay constant.

### 1.3.3 Control masses and control volumes

Another way to classify systems is as either a *control mass* or a *control volume*. This terminology is particularly common in engineering thermodynamics.

A control mass is a system which is defined to consist of a specified piece or pieces of matter. By definition, no matter can enter or leave a control mass. If the matter of the control mass is moving, then the system boundary moves with it to keep it inside (and matter in the environment outside).

A control volume is a system which is defined to be a particular region of space. Matter and energy may freely enter or leave a control volume, and thus it is an open system.

#### 1.4 A Note on Units

In this book, the SI system of units will be used exclusively. If you grew up anywhere but the United States, you are undoubtedly very familiar with this system. Even if you grew up in the US, you have undoubtedly used the SI system in your courses in physics and chemistry, and probably in many of your courses in engineering.

One reason the SI system is convenient is its simplicity. Energy, no matter what its form, is measured in Joules  $(1 \text{ J} = 1 \text{ kg-m}^2/\text{s}^2)$ . In some other systems, different units are used for thermal and mechanical energy: in the English system a BTU ("British Thermal Unit") is the unit of thermal energy and a ft-lbf is the unit of mechanical energy. In the cgs system, thermal energy is measured in calories, all other energy in ergs. The reason for this is that these units were chosen before it was understood that thermal energy was like mechanical energy, only on a much smaller scale. <sup>2</sup>

Another advantage of SI is that the unit of force is indentical to the unit of (mass x acceleration). This is only an obvious choice if one knows about Newton's second law, and allows it to be written as

$$\mathbf{F} = m\mathbf{a}.\tag{1.1}$$

In the SI system, force is measured in kg-m/s<sup>2</sup>, a unit derived from the 3 primary SI quantities for mass, length, and time (kg, m, s), but given the shorthand name of a "Newton." The name itself reveals the basis for this choice of force units.

The units of the English system were fixed long before Newton appeared on the scene (and indeed were the units Newton himself would have used). The unit of force is the "pound force" (lbf), the unit of mass is the "pound mass" (lbm) and of course acceleration is measured in  $ft/s^2$ . So Newton's second law must include a dimensional constant which converts from Ma units (lbm  $ft/s^2$ ) to force units (lbf). It is usually written

$$\mathbf{F} = \frac{1}{g_c} m \mathbf{a},\tag{1.2}$$

where

$$g_c = 32.1739 \text{ ft-lbm/lbf-s}^2.$$
 (1.3)

Of course, in SI  $g_c = 1$ .

 $<sup>^{2}</sup>$ Mixed unit systems are sometimes used too. American power plant engineers speak of the "heat rate" of a power plant, which is defined as the thermal energy which must be absorbed from the furnace to produce a unit of electrical energy. The heat rate is usually expressed in BTU/kw-hr.

In practice, the units in the English system are now *defined* in terms of their SI equivalents (e.g. one foot is defined as a certain fraction of a meter, and one lbf is defined in terms of a Newton.) If given data in Engineering units, it is often easiest to simply convert to SI, solve the problem, and then if necessary convert the answer back at the end. For this reason, we will implicitly assume SI units in this book, and will not include the  $g_c$  factor in Newton's 2nd law.