

1 Introduction

1.1 The Role of Thermodynamics

With an important restriction, the discipline of thermodynamics extends classical dynamics to the study of systems for which internal, microscopic, modes of motion are important. In dynamics, we are concerned about the macroscopic motion of matter. In thermodynamics it is motion at the microscopic level that mostly absorbs our interest. In dynamics we use the concepts of kinetic and potential energy and work to describe motion. In thermodynamics we add to these concepts internal energy and heat transfer, along with related properties such as temperature, pressure, and chemical potential. The important restriction, which we will discuss in detail later, is that thermodynamics is limited to analyzing changes between equilibrium states. Systems for which internal modes of motion are important include power generation, propulsion, refrigeration, chemical processes, and biology.

The goal of applied thermodynamic analysis is to understand the relationship between the design parameters and the performance of such systems, including specification of all appropriate state properties and energy flows. This task may be cast in terms of the following steps:

1. Identify any process or series of processes including components of cyclic processes.
2. Select control masses or volumes as appropriate.
3. Identify interactions between subsystems (i.e. work, heat transfer, mass transfer).
4. Sketch a system diagram showing control surfaces and interactions and a process diagram showing state changes.
5. Obtain all necessary properties at each state given sufficient independent properties – for example u, v, h, s, T, p , and chemical composition.
6. Calculate interactions directly where possible.
7. Apply the 1st Law to any process or set of processes.
8. Calculate the behavior of an isentropic process or a non-isentropic process given the isentropic efficiency.
9. Put it all together and solve the resulting system of nonlinear algebraic equations.
10. Calculate the system performance, including 2nd Law performance.

Most of these tasks are addressed in undergraduate engineering thermodynamics, at least for systems involving simple compressible substances as the working fluid.

However, the level of conceptual understanding necessary to address more complex substances and to understand and carry out 2nd Law performance analysis is usually left for graduate study. This is the focus of this book.

1.2 The Nature of Matter

As we know, matter is composed of atoms and molecules. The typical small atom is composed of a positively charged nucleus and negatively charge electrons. The nucleus, in turn, is composed of positively charged protons and neutral neutrons. The charge on electrons and protons is 1.602×10^{-19} C. It is the electrostatic forces that arise from charged electrons and protons that hold atoms together, allow for the formation of molecules, and determine the overall phase of large collections of atoms and/or molecules as solid, liquid, gas, or plasma. The spatial extent of electrostatic forces for a typical small atom is approximately 5 \AA or 5×10^{-10} m. There are about 2×10^9 atoms per lineal meter in a solid, resulting in about 8×10^{27} atoms/solidus m^3 . Thus, macroscopic systems are composed of a very large number of atoms or molecules.

In macroscopic systems, we describe behavior using the equations of motion derived from Newton’s Law. In principle, we should be able to solve the equations of motion for each atom or molecule to determine the effect of microscopic modes of motion. However, even if we ignore the fact that the behavior of individual atoms and molecules is described by quantum mechanics, it would be impossible to simultaneously solve the enormous number of equations involved. Clearly, an alternative approach is required as some kind of averaging must take place. Fortunately, nature has been kind in devising the laws of averaging in ways that allow for great simplification (although we will explore solving the classical equations of motion for small subsets of atoms as a way of estimating thermodynamic and other properties).

Thus, the solution of thermodynamics problems breaks down into two great tasks. The first is developing the rules for macroscopic behavior, given basic knowledge of microscopic behavior. We call this subject classical or macroscopic thermodynamics. Providing microscopic information is the subject of statistical or microscopic thermodynamics.

1.3 Energy, Work, Heat Transfer, and the 1st Law

The basis of the concepts of energy, kinetic and potential, and work can be derived from Newton’s Law:

$$\vec{F} = m\vec{a} \tag{1.1}$$

Consider applying a force to a macroscopic body of mass m , causing it to follow some trajectory. Integrating Newton’s Law over the trajectory, we obtain

$$\int_{\vec{x}_1}^{\vec{x}_2} \vec{F} d\vec{x} = \int_{\vec{x}_1}^{\vec{x}_2} m \vec{a} d\vec{x} = \int_{\vec{x}_1}^{\vec{x}_2} m \frac{d\vec{V}}{dt} d\vec{x} = \int_{\vec{V}_1}^{\vec{V}_2} m \vec{V} d\vec{V} = \frac{1}{2} m (V_2^2 - V_1^2) \quad (1.2)$$

We normally identify

$$W_{12} = \int_{\vec{x}_1}^{\vec{x}_2} \vec{F} d\vec{x} \quad (1.3)$$

as the work done during the process of causing the mass to move from point \vec{x}_1 to \vec{x}_2 . The work will depend on the path function $\vec{F}(\vec{x})$. Indeed, different functions can result in the same amount of work. As a result, we say that work is a path, or process integral.

In contrast, the integral of $m\vec{a}$ depends only on the value of the velocity squared at the end points. We identify

$$KE = \frac{1}{2} m V^2 \quad (1.4)$$

as the kinetic energy. The energy is a point or state property, and the integral of $\frac{1}{2} m dV^2$ is an exact differential.

The concept of potential energy arises out of the behavior of a body subject to a potential force field. A potential field is one in which the force imposed on the body is a function of position only. Gravity is the most common example of a potential field encountered in practice. Consider the case where a body subjected to an applied force is in a gravitational field whose effect is the constant weight W . If the gravitational field operates in the z direction, then Newton's Law takes on the form

$$F_z - W_z = ma_z \quad (1.5)$$

In the absence of an applied force, $W_z = ma_z$. Defining g as the effective acceleration due to gravity, $W_z = mg$. Adding this to the applied force and integrating as above gives

$$W_{12} - mg(z_2 - z_1) = \frac{1}{2} m (V_2^2 - V_1^2) \quad (1.6)$$

Note that the integral of the potential force term is in an exact form, and depends only on the value of mgz at the end points. Therefore, we normally call

$$PE = mgz \quad (1.7)$$

the potential energy, and write Eqs (1.1)–(1.6) as

$$\frac{1}{2} m (V_2^2 - V_1^2) + mg(z_2 - z_1) = W_{12} \quad (1.8)$$

or

$$\Delta E = \Delta KE + \Delta PE = W_{12} \quad (1.9)$$

where

$$E = KE + PE \quad (1.10)$$

This is a statement of the 1st Law of Thermodynamics for a body with no internal energy. As can be seen, it means that energy can be viewed as a property that measures the ability of matter to do work. Furthermore, rather than the absolute value of the energy, the important quantity is the change in energy.

The concepts of work and energy can also be applied at the microscopic level. Atoms and molecules, and nuclei and electrons, can have kinetic energy, and the electrostatic fields within and between atoms can lead to potential energy. Furthermore, electrostatic forces can result in work being done on individual particles. If we identify the total kinetic and potential energy at the microscopic level as U , then the total energy of a macroscopic body becomes

$$E = U + KE + PE \tag{1.11}$$

Heat transfer is work carried out at the microscopic level. It arises from random individual molecular interactions occurring throughout a material or at a surface between two materials. The non-random, or coherent motion leads to macroscopic work, the random component leads to heat transfer. We typically identify heat transfer as Q , and the complete form of the 1st Law becomes

$$\Delta E = W_{12} + Q_{12} \tag{1.12}$$

or in differential form

$$dE = \delta W + \delta Q \tag{1.13}$$

where δ indicates that work and heat transfer are path functions, not exact differentials.

1.4 Equilibrium

As mentioned in the first paragraph of this book, thermodynamics involves the study of systems that undergo change between a set of very restricted states called equilibrium states. Equilibrium is the stationary limit reached by some transient process and one must establish that equilibrium is reached and thermodynamic analysis can be used. As we shall see, the statistics of large numbers lead to great simplifications when considering stationary or equilibrium states.

At the microscopic level processes are usually very fast. Typical internal motions such as rotation or vibration occur with periods of 10^{-12} – 10^{-15} sec. In a gas, collisions occur every few 10^{-9} – 10^{-12} sec. Thus, internal modes tend to want to be in equilibrium, at least locally. At the macroscopic level, however, processes such as flow, heat transfer, and mass transfer can be quite slow. Table 1.1 lists various processes and characteristic times for them to occur. When it is necessary to understand the system behavior while these transient processes are occurring, one must use the principles of fluid mechanics, heat transfer, mass transfer, and so on. (Here, L is a characteristic length, V a characteristic velocity, α the thermal diffusivity, and D the mass diffusivity.)

This leads to a very important concept, that of “local thermodynamic equilibrium” (LTE). If local molecular relaxation processes are very fast compared to

Table 1.1 Characteristic times of transport processes

Process	Characteristic time
Flow	L/V
Heat transfer	L^2/α
Mass transfer	L^2/D

the characteristic times of Table 1.1, then locally within the flow thermodynamic equilibrium will hold, allowing the use of all the normal thermodynamic relationships. Indeed, this approximation holds for almost all flow, heat transfer, and mass transfer processes that are normally encountered, with the exception of very highspeed flows.

1.5 Thermodynamic Properties

Properties are quantities that describe the state of a system. Position, rotational orientation, and velocity, for example, describe the instantaneous dynamic state of a solid body. In thermodynamics we are concerned with problems involving work and heat transfer. Therefore, energy must be an important property, as it is a measure of the ability of matter to do work or transfer heat. Work and heat transfer are dynamic quantities and not descriptive of the state of a system. However, the amount of work or heat transfer required to bring a system to a given state will clearly be influenced by the size of the system, and thus volume and mass are also important thermodynamic properties. Composition is also an important property, as it will clearly affect the microscopic behavior of a system. To summarize, we have identified energy, volume, and mass (or moles) as important properties. For a multicomponent system we must also specify either the mass or moles of each specie or phase present.

The properties thus identified, U , V , and N_i (where N_i is the number of moles of component i), have an important feature in common. They are all properties that are extensive in nature. By that we mean that they are a measure of the size of the system. And, in fact, were the size of a system to change, all other things being held constant, each of these properties would change by the same amount. We thus formally call them extensive properties. If, for a closed system, the extensive properties U , V , and N_i are specified, then the thermodynamic state is completely specified.

In addition to the extensive properties, we shall be concerned with several intensive properties. Intensive properties are properties that do not scale with the size of a system, but rather are a function of the normalized extensive properties. Temperature and pressure are examples of important intensive properties. As we shall see, the intensive properties are each paired with a related extensive property, and are defined in terms of the extensive properties.

The extensive properties can be cast in an intensive form by normalization, usually in terms of the volume or total mass or moles. However, as we shall see, they remain fundamentally different in character from the true intensive properties.

1.6 The Fundamental Problem of Thermodynamics

There are four types of thermodynamic problems. These are:

- 1. Initial state/final state problems. Involve specifying the initial states of two or more subsystems that may include reservoirs. Work, heat transfer, or mass transfer is then allowed and the final states of the subsystem determined.
- 2. Specified interaction problems. In specified interaction problems, one specifies the nature and value of interactions of a system with its surroundings. Consider compressing a gas in an insulated piston cylinder arrangement. If the initial state of the gas and the work done in compression are specified, then one can calculate the final state of the gas.
- 3. Limiting process problems. In this case, the initial and final state of a system are specified, and the maximum or minimum amount of heat transfer or work required is obtained. Predicting the maximum output of an ideal gas turbine is an example.
- 4. Cycle analysis. The analysis of a cyclical sequence of processes, such as the Rankine vapor power cycle.

In fact, each of the above problems is a subset of the first. Consider the adiabatic cylinder shown in Fig. 1.1. A piston separates the cylinder into two subsystems. Several possibilities can occur:

- 1. The piston is adiabatic, fixed, and impermeable.
- 2. In the language of thermodynamics, the piston becomes diathermal. This means that heat transfer can occur through the piston.
- 3. The piston is now allowed to move. Thus, work can take place.
- 4. The piston becomes porous. Mass transfer is allowed.

The first case means that the system is completely closed to any kind of interaction, and if the subsystems are individually in equilibrium they remain so. Each additional change removes a constraint and results in a possible spontaneous process leading to a new



Figure 1.1 The fundamental problem.

equilibrium state. The fundamental problem of thermodynamics is to find the final state once a given constraint is removed. If the fundamental problem can be solved, then type 1–4 problems can also be solved.

Once it is possible to solve the fundamental problem, then all other types of thermodynamic system problems can be solved by breaking the system down into its component processes and analyzing each process individually. This will usually result in a simultaneous set of nonlinear algebraic equations.

1.7 Analysis of Non-equilibrium Behavior

As we have seen, thermodynamics is the study of equilibrium states. That is, given a change in system constraints, what new equilibrium state arises? Thermodynamics does not address the nature of the process or processes that result in a change in equilibrium state. The dynamics part of the word thermodynamics is thus something of a misnomer. Many workers have suggested using the word thermostatics. However, two centuries of usage are not easily put aside, and our use of the name thermodynamics is unlikely to change. More common is to use the term equilibrium thermodynamics.

The question naturally arises, how do we deal with processes and non-equilibrium states? This is the subject of kinetic theory, which leads to the disciplines of fluid mechanics, heat transfer, and mass transfer. As we shall see from our study of microscopic thermodynamics, the equilibrium state arises from the statistical averaging of the possible microscopic states allowed by the macroscopic constraints. In complete forms of kinetic theory equations are derived that describe the departure of these state relations from equilibrium. For example, in a gas there is a unique distribution of atomic velocities that occurs at equilibrium. For momentum transport or heat transfer to occur, this distribution must depart from its equilibrium form. We will explore this subject in a later chapter.

1.8 Summary

In this chapter we explored some of fundamental concepts upon which the field of thermodynamics rests. We started with a short discussion of how matter is composed of atoms and molecules, and that the average motions of these particles at the microscopic level has important implications at the macroscopic level.

Essential to understanding thermodynamics are the concepts of energy, work, heat transfer, and the 1st Law. Work, of course, is a force acting through a distance:

$$W_{12} = \int_{\vec{x}_1}^{\vec{x}_2} \vec{F} \cdot d\vec{x} \tag{1.14}$$

Using Newton’s Law $\vec{F} = m\vec{a}$ we derived the concept of kinetic energy as

$$\int_{\vec{x}_1}^{\vec{x}_2} \vec{F} d\vec{x} = \frac{1}{2}m(V_2^2 - V_1^2) \tag{1.15}$$

or

$$KE = \frac{1}{2}mV^2 \tag{1.16}$$

After some manipulation, we also derived the potential energy

$$PE = mgz \tag{1.17}$$

Putting these concepts together results in the 1st Law of Thermodynamics

$$\Delta E = \Delta KE + \Delta PE = W_{12} \tag{1.18}$$

Adding in the possibility of kinetic energy and work taking place at the microscopic level, the 1st Law becomes

$$\Delta E = U + KE + PE = W_{12} + Q_{12} \tag{1.19}$$

Work and heat transfer are processes that depend on the details, or path, by which they take place. Internal, kinetic, and potential energies, on the other hand, are properties related to the amount of work or heat transfer that takes place. In addition, the composition of any working substance is important as well.

Finally, one can cast all thermodynamic problems in terms of the fundamental problem described in Section 1.6. We explore this in detail in Chapter 2.

1.9 Problems

- 1.1 Compare the kinetic energy of a 0.5-km diameter asteroid approaching the Earth at 30,000 m/sec with the 210,000 TJ released by a 50-megaton hydrogen bomb.
- 1.2 Calculate the potential energy required for a 160-lbm person to hike to the top of Long’s Peak (14,259 ft) from downtown Boulder, CO (5,430 ft). Compare that to the energy in a McDonald’s large Big Mac Meal with chocolate shake.
- 1.3 Estimate the number of molecules in the Earth’s atmosphere.
- 1.4 Calculate the number of molecules in one cubic meter of air at STP. Then estimate the total kinetic energy of this mass assuming that the average speed of molecules is the speed of sound in air at STP. Compare this to the potential energy associated with lifting this mass of air 20 m.
- 1.5 Consider two equal 1000-cm³ cubes of copper. Initially separated, one has a temperature of 20 °C and the other is at 100 °C. They are then brought into contact along one wall, but otherwise isolated from their surroundings. Estimate how long it will take for the two cubes to come into equilibrium.