Fundamentals of Thermal Physics

An Introduction to Modern Thermodynamics
with Statistical Mechanics

Gabriel J. Williams, Jr.
1/5/2016

Table of Contents

Chapter 1: Preliminaries

1.1 What is Thermal Physics?

Thermal physics is the study of two closely related subjects: **thermodynamics** and **statistical mechanics**. Thermodynamics is a general theory of macroscopic systems which provides limits on allowable physical processes involving energy transformations and relations between measurable quantities. The relevant physical systems are called **thermodynamic systems**. A thermodynamic system is a macroscopic portion of the universe, by which we mean that it consists of a very large number of more elementary constituents, each of which is able to carry mechanical energy. In contrast, the rest of the universe is called the **environment** and the separation between the system and the environment is generally assumed to occur via a boundary separating the two.

Every thermodynamic system is able to store energy by virtue of the fact that the elementary constituents of a thermodynamic system possess mechanical energy. A fundamental objective of thermodynamics is to describe the interaction of such a system with the environment or the interaction between different systems among themselves. Such interactions inevitably lead to an exchange of energy between them and there are broadly two ways in which this can occur: (i) either energy enters or leaves the system because an external mechanical constraint is changed (this occurs, for example, when a gas expands or is compressed and its volume changes) or (ii) energy spontaneously moves across the boundary by transfer on the molecular level (for instance, when a hot body is brought in contact with a cold body). We say that the first kind of energy transfer occurs by **useful work**, while the second occurs by **heat**.

Thus, it can be said that thermodynamics is the area of physics that deals with the transformation of heat into useful work (and vice versa), and how these quantities are related to the measurable properties of a physical system. The possibility of transforming heat into useful work and vice-versa had been recognized for a very long time, in fact even before the nature of heat was understood. Heat was originally supposed to be a kind of fluid, called "caloric", flowing from one body to another. This understanding was replaced in the mid-19th century by the more modern mechanical theory of heat –thanks to the work of Mayer, Joule, Maxwell, Boltzmann and others. Today we understand it as energy exchanged between macroscopic systems in any way that does not involve mechanical work.

Since every macroscopic system is made up of elementary constituents, exchanges of energy must eventually be mechanical processes on the microscopic scale. Therefore, thermodynamics is a special branch of mechanics – the mechanics of a large number of elementary constituents interacting with each other. However, the task of solving the equations of motion for more than two interacting particles becomes an extremely difficult, if not impossible task. The general N body problem contains $6N$ variables. Subtracting the ten first integrals of the motion (one for energy, three for the motion of the center of mass, three for the total momentum, three for the total angular momentum) leaves us with $6N - 10$ variables, subject to the same number of initial conditions, to contend with. If the system has on the order of Avogadro's number $N_A = 6.023 \times 10^{23}$ of elementary constituents (such as 1 mole of oxygen), then the problem is computationally infeasible, even assuming that the initial conditions could all be obtained experimentally, which itself is quite infeasible.

However, it should be noted that even if such a solution could be obtained, it would give us information that is far in excess of what we can reasonably measure or control. In fact, we are able in practice to impose only very coarse constraints on a macroscopic system and to measure only a very small number of its properties (such as pressure, volume, and temperature) compared to the number of mechanical variables involved in a microscopic treatment. The treatment via mechanics, even if it could be accomplished, would therefore be quite useless from a practical standpoint. An alternative method, originally proposed by Boltzmann, is to treat the mechanical system statistically i.e., asking questions about the average behavior of the system rather than the detailed questions concerning the motion of the individual constituents. This microscopic approach, combining mechanics and statistics, leads to **statistical mechanics**.

Because we measure and control a small number of properties of the system, some of which are related only statistically to its underlying microscopic properties, it is worth asking how far we can go if we simply ignore the underlying mechanics. This is the approach of **classical thermodynamics**, which concentrates only on relationships between the measurable properties of the system. This requires us to define clearly the thermodynamic variables we use in our description of the macroscopic system by describing instruments to precisely measure them. Once this is accomplished, the sole task of thermodynamics is to codify experiment by postulating a set of principles relating these thermodynamic variables. In essence, this means that thermodynamics is the study of systems whose elementary constituents are so large that fluctuations about their average behavior can be completely ignored.

In thermal physics, our goal is to understand the properties of macroscopic systems, that is, systems of many electrons, atoms, molecules, photons, or other constituents. Examples of familiar macroscopic objects include systems such as the air in your room, a glass of water, a coin, and a rubber band – examples of a gas, liquid, solid, and polymer, respectively. Less familiar macroscopic systems include superconductors, cell membranes, the brain, and neutron

stars. We will find that the type of questions we ask about macroscopic systems differ in important ways from the questions we ask about systems that we treat microscopically. For example, consider the air in your room. Have you ever wondered about the trajectory of a particular molecule in the air? Would knowing that trajectory be helpful in understanding the properties of air? Instead of questions such as these, examples of questions that we do ask about macroscopic systems include the following:

1. How does the pressure of a gas depend on the temperature and the volume of its container?
2. How does a refrigerator work? How can we make it more efficient?
3. How much energy do we need to add to a kettle of water to change it to steam?
4. Why are the properties of water different from those of steam, even though water and steam consist of the same type of molecules?
5. How and why does a liquid freeze into a particular crystalline structure?
6. Why does helium have a superfluid phase at very low temperatures? Why do some materials exhibit zero resistance to electrical current at sufficiently low temperatures?
7. In general, how do the properties of a system emerge from its constituents?

These questions can be roughly classified into two groups. Questions 1–3 are concerned with macroscopic properties such as pressure, volume, and temperature and processes related to heating and work. These questions are relevant to thermodynamics which provides a framework for relating the macroscopic properties of a system to one another. Thermodynamics is concerned only with macroscopic quantities and ignores the microscopic variables that characterize individual molecules. For example, we will find that understanding the maximum efficiency of a refrigerator does not require a knowledge of the particular liquid used as the coolant. Many of the applications of thermodynamics are to engines, for example, the internal combustion engine and the steam turbine.

Questions 4–7 relate to understanding the behavior of macroscopic systems starting from the atomic nature of matter. For example, we know that water consists of molecules of hydrogen and oxygen. We also know that the laws of classical and quantum mechanics determine the behavior of molecules at the microscopic level. The goal of statistical mechanics is to begin with the microscopic laws of physics that govern the behavior of the constituents of the system and deduce the properties of the system as a whole. Statistical mechanics is a bridge between the microscopic and macroscopic worlds.

Both approaches have their advantages and disadvantages. In the microscopic approach (statistical mechanics) the system must be modeled mechanically in a fairly detailed fashion. Our understanding of the system in statistical mechanics is more profound, but the mathematical difficulties involved in the actual transition from theoretical model to experimental predictions

and vice versa are also greater. In the macroscopic approach (classical thermodynamics), as conceived by Mayer, Carnot, Clausius, Kelvin and many others, our understanding of the actual processes between the elementary constituents is sacrificed for mathematical simplicity. It is remarkable indeed that many deep results can yet be obtained without any reference whatsoever to the underlying mechanics. This must be understood as evidence of the power of statistical averaging: when very large numbers are involved statistical fluctuations become vanishingly small and classical thermodynamics becomes an excellent effective theory. This being said, it cannot be forgotten that, although an effective theory, thermodynamics is complete and internally consistent within its realm of applicability.

Although statistical mechanics and thermodynamics are central to many research areas in physics (such as high energy physics, astrophysics, atmospheric physics, biophysics, geophysics, and condensed matter physics), both have had less of a presence in the undergraduate curriculum than classical mechanics, electromagnetism, and quantum mechanics. It wasn't many years ago that statistical mechanics was not even part of the undergraduate physics curriculum at many colleges and universities. The notes are an effort to bring some of the recent advances in research in modern thermodynamics and statistical mechanics into the undergraduate curriculum.

1.2 Thermodynamic Systems
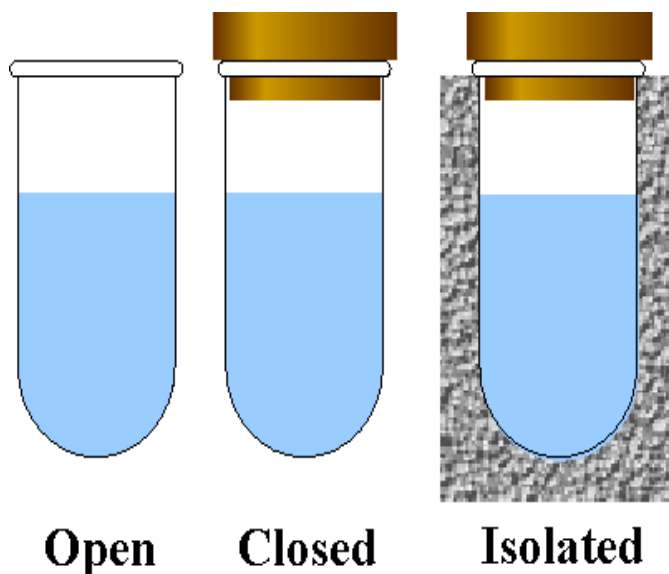
Figure 1.1 Schematic of the three basic types of thermodynamic systems

As discussed above, a fundamental objective of thermodynamics is to describe the interaction of a thermodynamic system with its environment or the interaction between different thermodynamic systems among themselves. For this reason, a thermodynamic system can be

classified based on how the environment affects the thermodynamic system. In general, there are three types of thermodynamic systems:

- **Open systems**: Thermodynamic systems which can exchange both matter and energy with its environment.
- **Closed systems**: Thermodynamic systems which can only exchange energy with its environment.
- **Isolated systems**: Thermodynamic systems which can exchange neither energy nor matter with its environment.
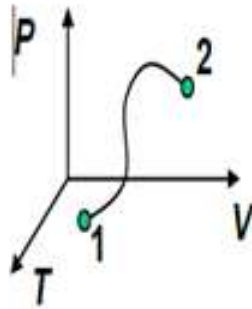
Figure 1.2 Schematic of a thermodynamic process in thermodynamic phase space

Thermodynamic systems are typically examined by studying its thermodynamic state. A **thermodynamic state** is the macroscopic condition of a thermodynamic system as described by the values of a small number of variables, such as the temperature, pressure, density, volume, composition and others that will be defined later. These variables are called the **state variables** of the system and they are used to fully specify a given thermodynamic system. They are always few in number when compared to the number of mechanical variables that would be required, and generally may be strictly defined only when the system is in **equilibrium,** which occurs when there is no change of the state variables in time. The state variables for a given thermodynamic system span the **thermodynamic phase space** of the system. This means that the collection of state variables in the thermodynamic phase space defines a space of possible **equilibrium states** of the system. An essential task of thermodynamics is to discover a reasonably "complete" set of state variables for the given system.

The evolution of thermodynamic states is typically examined by studying thermodynamic processes. A **thermodynamic process** is any process that takes a macroscopic system from one equilibrium state to another. Therefore, a thermodynamic process is any process that produces a continuous curve in thermodynamic phase space, as shown in Figure 1.2. Broadly speaking, thermodynamic processes may be divided into two classes: **quasi-static processes** and **non**

quasi-static processes. We can motivate these classes of processes by considering the following examples.
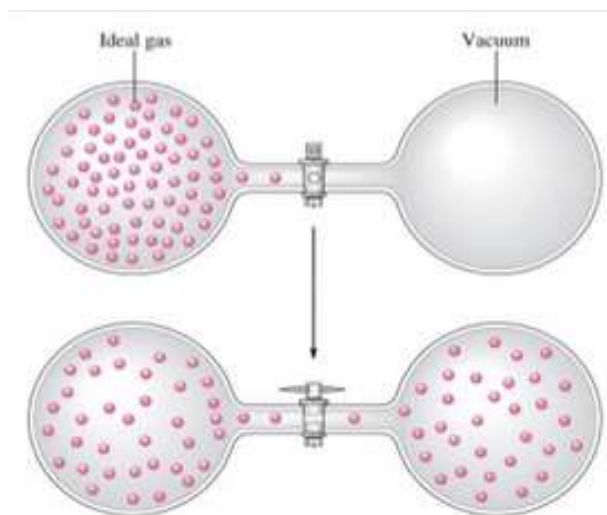
Figure 1.3 Free expansion of a gas into a vacuum

Consider a gas which is enclosed inside a container of volume V_1. Suppose that the container has a stopcock which is closed but which may be opened at any time and that the container is itself enclosed inside a larger container of volume V_2 which is vacuous. Let's wait for long enough so that the gas inside V_1 is in equilibrium and then suddenly open the stopcock, as shown in Figure 1.3. The gas will immediately rush out of the opening and fill the entire volume V_2. For a time after the stopcock is opened, the gas is not in an equilibrium state; in fact, the variables P, V, and T cannot be measured because measuring them requires equilibrium. The gas is said to be in a **dynamical state**. Yet, if we wait long enough the gas will achieve a new equilibrium state with a new pressure, volume, and temperature. Therefore, the process of free expansion has transformed the gas from one equilibrium state to another equilibrium state, but the process *itself* cannot be described by the equilibrium variables. This is one example of a thermodynamic process called a **non-quasi-static** process.

Because the process described above cannot be described by the equilibrium variables, classical thermodynamics (which relies on relationship between equilibrium variables) will have little to say about it. However, suppose the gas is made to expand so slowly that it can be treated *as though* it is always in equilibrium. To accomplish this, imagine opening the stopcock for a very short interval of time so that only an infinitesimal quantity of gas is released and then wait for the system to come to equilibrium. If we repeat this process a large number of times, then we will end up with a final equilibrium state that will in general *not* be the same as the state we ended up with in the first process. Nevertheless, we still have a thermodynamic process taking the system from an initial equilibrium state to a final equilibrium state, and this process occurs

slowly enough that the gas may always be considered to exist in equilibrium. This process is called a **quasi-static** process.

1.3 Temperature

We have an intuitive understanding of temperature in terms of "hot" and "cold" or as a number we can read on a thermometer. For the purposes of classical thermodynamics, we use a more precise definition.

1.3.1 Zeroth Law of Thermodynamics

We are all familiar with the fact that two objects at different initial temperatures eventually reach some intermediate temperature when placed in contact with each other. To understand the concept of temperature, it is useful to define two often used phrases: **thermal contact** and **thermal equilibrium**. To grasp the meaning of thermal contact, let us imagine that two objects are placed in an insulated container such that they interact with each other but now with the rest of the world (i.e. a closed system). If the objects are at different temperatures, energy is exchanged between them, even if they are initially not in physical contact with each other. **Heat is the transfer of energy from one object to another as a result of a difference in temperature between the two.** We shall examine the concept of heat in greater detail in the next chapter, but for the purposes of the current discussion, we assume that two objects are in **thermal contact** with each other if energy can be exchanged between them. **Thermal equilibrium** is a situation in which two objects in thermal contact with each other cease to exchange energy by the process of heat.
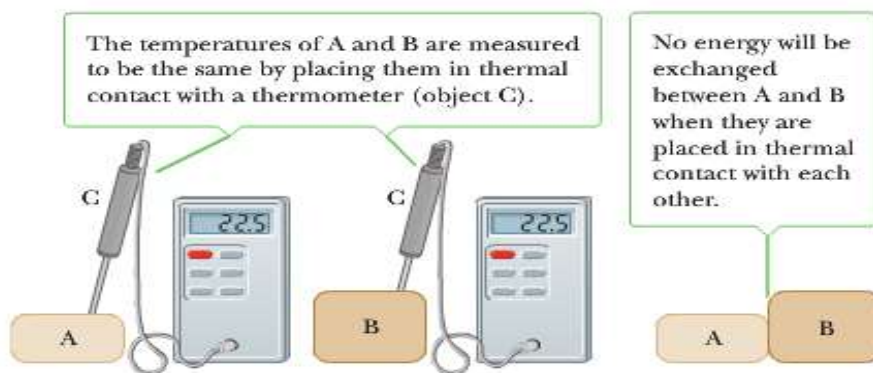
Figure 1.4 Schematic of two objects A and B in thermal equilibrium with a third object C

Consider two thermodynamic systems, A and B, one of which is "hotter" than the other. Suppose that we bring them into thermal contact with one another, allowing them only to exchange energy through an immovable partition so that no mechanical work is done by one

system on the other. Over a period of time, the "hotter" system becomes "colder" and the "colder" system becomes "hotter" until finally, after a very long time (which depends on the composition of the systems), the net exchange of energy stops and the two bodies are equally "hot". At this point they have ceased to exchange energy between themselves on average and the systems are in thermal equilibrium. How can we verify and determine that these two systems are truly in thermal equilibrium? This answer is supplied by the so-called **zeroth law of thermodynamics** which states that:

If two thermodynamic systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

Thus, in order to determine if systems A and B are in thermal equilibrium, we introduce a third system C (i.e. a thermometer) as shown in Figure 1.4. The zeroth law of thermodynamics states that if A is in thermal equilibrium with C and if B is in thermal equilibrium with C, then A *must* be in thermal equilibrium with B. The zeroth law of thermodynamics ensures us that thermal equilibrium is determined by a single variable. We call this variable the temperature and so we may give the following definition of the temperature:

Temperature is that variable of thermodynamic systems, whose equality ensures that that they are in thermal equilibrium and whose inequality ensures that they are not in thermal equilibrium with each other.

Systems that are not in thermal equilibrium with each other will exchange energy between themselves if they are brought in contact with one another, even if no mechanical work is done in the process. This suggests that heat is connected with temperature gradients between two systems or between a system and its environment.

1.3.2 Thermometers and Temperature Scales

With this operational definition of temperature, we now ask how we should quantify it. There are many properties of matter that depend on temperature and that can be measured directly. For example, we know that materials expand and contract when heated and cooled respectively at fixed pressure, so length, area and volume which can be measured geometrically are examples of such properties. Likewise, the pressure of a gas kept at a fixed volume will increase with increasing temperature, so pressure is also such a property. Another example would be the electrical resistance of materials which grows with temperature. Properties of materials which change with temperature are called **thermometric properties**.

We can use thermometric properties to build thermometers as follows. Let *X* be the thermometric property of some material we wish to turn into a thermometer. We simply *define*

the scale of temperature in such a way that the variation of the thermometric property is a linear function of the temperature, then

$$X(T) = X_0 + \alpha^{-1}(T - T_0)$$

Inverting the above equation gives us,

$$T(X) = T_0 + \alpha(X - X_0)$$

The two constants, α and X_0, that define this linear scale must be fixed by choosing two phenomena which are known to always occur at the same temperature and which are very easily reproducible. Two quantities that fit these criteria are the boiling point of pure water at sea level and the triple point of pure water (i.e., when water coexists in equilibrium with water vapor and ice) at sea level. Let's call the temperatures associated with these events T_b and T_f, respectively, and the values of X associated with these events X_b and X_f, respectively. Replacing (X_0, T_0) with (X_f, T_f) gives

$$T_b = T_f + \alpha(X_b - X_f) \Rightarrow \alpha = \frac{T_b - T_f}{X_b - X_f}$$

Therefore, we have

$$T = T_f + \frac{T_b - T_f}{X_b - X_f}(X - X_f)$$

Since the thermometric property, X, is easily measured, we can measure and fix the values of X_b and X_f. We finish setting up the temperature scale by choosing convenient values for T_b and T_f. Historically, the first thermometer which used pure water chose $T_f = 0$ and $T_b = 100$, producing the **Celsius scale** named after the Swedish astronomer Anders Celsius $(1701 - 1744)$

$$T^{(C)} = \frac{100}{X_b - X_f}(X - X_f)$$

Alternatively, by choosing $T_f = 32$ and $T_b = 212$, we obtain the **Fahrenheit scale**, named after the German physicist Daniel Gabriel Fahrenheit

$$T^{(F)} = 32 + \frac{180}{X_b - X_f}(X - X_f)$$

For a historical perspective of the development of the Fahrenheit scale, see the following article: http://www.livescience.com/39916-fahrenheit.html. Both the Celsius and Fahrenheit scales are *linear* scales and can be directly compared to one another

$$T^{(C)} = \frac{5}{9}\left(T^{(F)} - 32\right)$$

It's important to note that there is nothing special about either of the scales and nothing special about the choice of fixed points. All that is important is to remember that they are *linear* scales. In general, we could choose the temperature to be a more complicated monotonic function with two arbitrary constants that could subsequently be determined as above. This would not lead to any new physics. The linear function is the simplest monotonic function and therefore the best choice.

1.3.3 The Thermodynamic Temperature Scale

Because we never prescribed the material or thermometric property that we would use, an implicit assumption that has been made in the above discussion is that the temperature can be defined as a linear function of *all* thermometric properties of *all* materials. Actually this is not the case, for if we were to assume a linear relationship between the temperature and a particular thermometric property of some material and construct a thermometer from it, we should find that another thermometric property of the same material or the same thermometric property of a different material would no longer be a linear function of the temperature as measured by our thermometer. We must therefore choose *one* thermometric property of one particular substance which we then take as our standard. The standard material chosen is an **ideal gas** (which will be precisely defined later). The standard thermometric property chosen is generally the pressure of the gas at constant volume and the thermometer so constructed is called a **constant volume gas thermometer**.
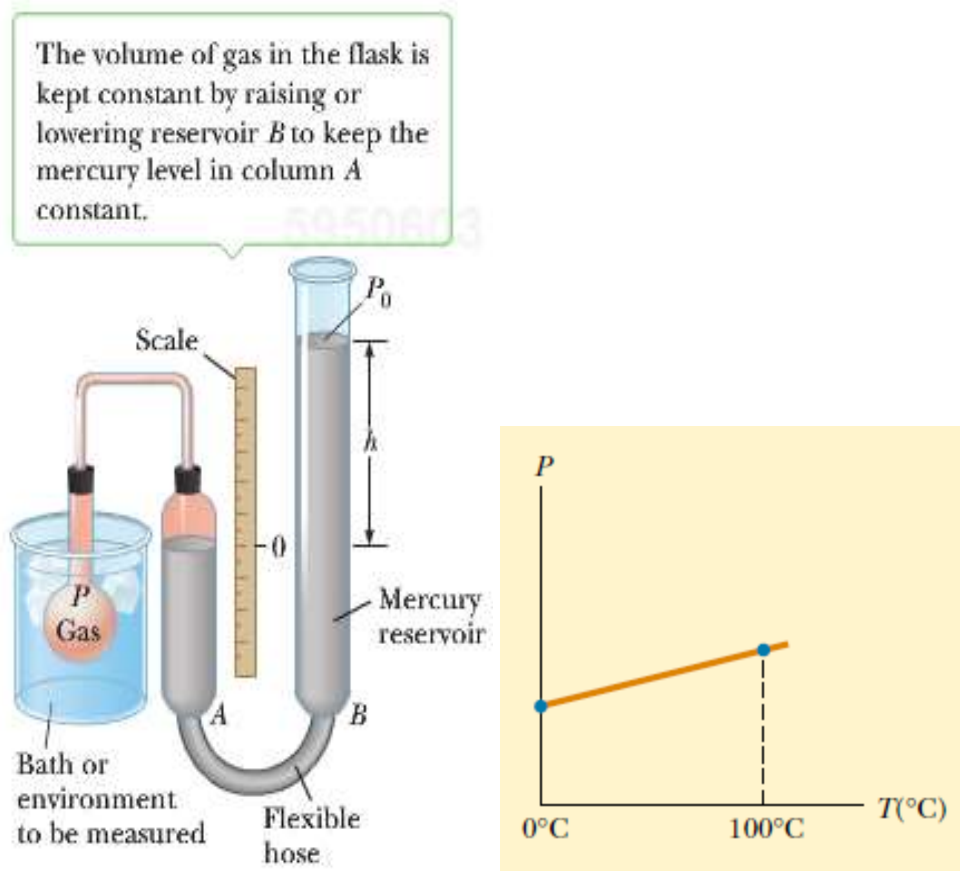
Figure 1.5 (Left) A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath. (Right) Pressure vs. temperature graph of the constant-volume gas thermometer

A constant volume gas thermometer is shown in Figure 1.5. The behavior observed in this device is the variation of pressure with temperature of a fixed volume of gas. When the constant-volume gas thermometer was developed, it was calibrated using the ice and steam points of water as follows: The gas flask is inserted into an ice–water bath, and mercury reservoir B is raised or lowered until the volume of the confined gas is at some value, indicated by the zero point on the scale. The height h, the difference between the levels in the reservoir and column A, indicates the pressure in the flask at 0°C. The flask is inserted into water at the steam point, and reservoir B is readjusted until the height in column A is again brought to zero on the scale, ensuring that the gas volume is the same as it had been in the ice bath (hence the designation "constant-volume"). A measure of the new value for h gives a value for the pressure at 100°C.

These pressure and temperature values are then plotted on a graph. The line connecting the two points serves as a calibration curve for measuring unknown temperatures. If we want to measure the temperature of a substance, we place the gas flask in thermal contact with the substance and adjust the column of mercury until the level in column A returns to zero. The

height of the mercury column tells us the pressure of the gas, and we could then find the temperature of the substance from the calibration curve.
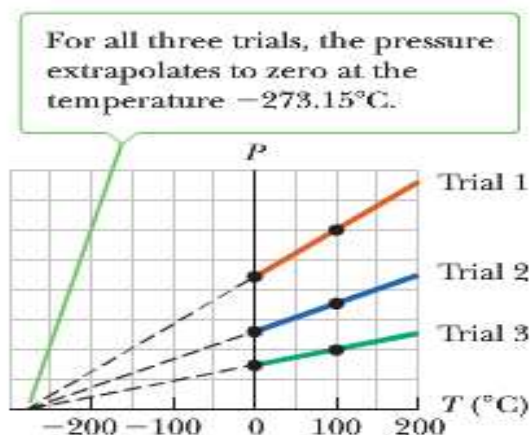
Figure 1.6 Pressure versus temperature for three dilute gases. Note that, for all gases, the pressure extrapolates to zero at the temperature -273.15°C

Now suppose that temperatures are measured with various gas thermometers containing different gases at different initial pressures. If we now plot the pressure vs. the temperature as measured by our thermometer for different gases as shown in Figure 1.6, we get straight lines similar to those shown in Figure 1.5. The different lines refer to the different (constant) volumes of the gases. Further experimentation shows that the thermometer readings are nearly independent of the type of gas used, as long as the gas pressure is low and the temperature is well above the point at which the gas liquefies. The agreement among thermometers using various gases improves as the pressure is reduced. Notice that in all cases the lines intersect the temperature axis at a fixed point, i.e., $T^{(C)} = -273.15$°C. At this temperature the pressure would be exactly zero. If we were to attempt to extend the line to the left, the pressure would end up being negative. Since pressure cannot be negative, we must consider the temperature -273.15°C to be the absolute minimum temperature attainable. This significant temperature is used as the basis for the **absolute temperature scale** (also known as the **Kelvin scale**), which set -273.15°C as its zero point. This temperature is often referred to as **absolute zero**. The size of a degree on the absolute temperature scale is identical to the size of a degree on the Celsius scale. Thus, the conversion between these temperatures is

$$T^{(C)} = T - 273.15$$

where T is the absolute temperature. The Kelvin scale employs the SI unit of absolute temperature, the **kelvin**, which is defined to be **1/273.15 of the difference between absolute zero and the temperature of the triple point of water**.

1.4 Properties of an Ideal Gas

In this section, we examine the properties of a gas of mass m confined to a container of volume V at a pressure P and a temperature T. It's useful to know how these quantities are related. In general, the equation that interrelates these quantities, called the **equation of state**, is very complicated. However, if the gas is maintained at very low pressure (or low density), the equation of state is quite simple and can be found experimentally. Such a low-density gas is commonly referred to as an **ideal gas**.

1.4.1 The Ideal Gas Law

It is convenient to express the amount of gas in a given volume in terms of the number of moles n. Recall that one mole of any substance is that amount of the substance that contains Avogadro's number $N_A = 6.022 \times 10^{23}$ of constituent particles (atoms or molecules). The number of moles n of a substance is related to its mass m through the expression

$$n = \frac{m}{M}$$

where M is the molar mass of the substance, which is usually expressed in units of grams per mole. The molar mass is the mass of one mole of a substance. For example, the molar mass of oxygen is 32.0 g/mol; therefore, the mass of one mole of oxygen is 32.0 g.
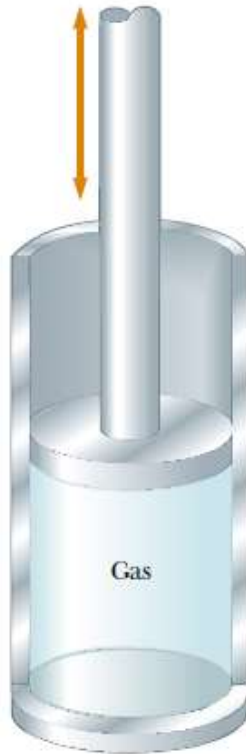
Figure 1.7 An ideal gas confined to a cylinder whose volume can be varied by means of a movable piston

Now suppose that an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston. If we assume that the cylinder does not leak, the mass (or the number of moles) of the gas remains constant. For such a system, experiments provide the following information.

- When the gas is kept at a constant temperature, its pressure is inversely proportional to its volume (also known as **Boyle's law**)
- When the gas is kept at a constant pressure, its volume is proportional to its temperature (also known as **Charles' law**)
- When the gas is kept at a constant volume, its pressure is proportional to its temperature (also known as **Guy-Lussac's law** or **Amonton's law**)
- When the gas is kept at a constant temperature and pressure, the volume of the gas is proportional to the number of moles in the gas (also known as **Avogadro's law**)

These relationships can be summarized as $PV \propto nT$. These observations indicate that there is a relationship between the pressure, volume, and temperature of ideal gases of the form $f(P, V, T) = 0$, where f is some function. This is known as an **equation of state** and it is a constraint equation that defines a hypersurface in the thermodynamic phase space of the thermodynamic state variables. In other words, an equation of state defines the surface in thermodynamic phase space in which all acceptable equilibrium states exist.

The equation of state which fits the observations given above is known as the ideal gas law:

$$PV = nRT \qquad (1.1)$$

In this expression, R is a universal constant that is the same for all low-density gases and T is the absolute temperature in kelvins. Experiments on numerous gases show that as the pressure approaches zero, the quanity PV/nT approaches the same value R for all gases. For this reason, R is called the **universal gas constant**. In SI units, $R = 8.315\,J/mol \cdot K$. Now that we have presented the equation of state, we are ready for a formal definition of an ideal gas: **An ideal gas is one for which PV/nT is constant at all pressures.**

The ideal gas law can be written in other forms commonly used by physicists. First, the ideal gas law can also be written in terms of the number of molecules N present in the gas. Because $N = nN_A$, we can write equation (1.1) as

$$PV = NkT$$

In this expression, $k = R/N_A = 1.38 \times 10^{-23}\,J/K$ is known as the **Boltzmann's constant**. Second the ideal gas law can be written in terms of the density ρ of the gas. Because $n = m/M$, we can write equation (1.1) as

$$P = \rho R^* T$$

In this expression, $R^* = R/M$ is known as the **specific gas constant** (since it varies depending on the type of gas being examined).

The ideal gas law is an approximation to the behavior of real gases. It is valid in the limit of low density, when the average space between gas molecules is much larger than the size of a molecule. For air (and other common gases) at room temperature and atmospheric pressure, the average distance between molecules is roughly ten times the size of a molecule, so the ideal gas law is accurate enough for most purposes. Furthermore, experiments show that the behavior of gases at very low densities is nearly independent of the molecular structure of the gas provided that the temperature is above the point at which the gas liquefies.

1.4.2 Dalton's Law of Partial Pressures

Although we have considered a pure gas, made of a single type of molecule, the above results can be generalized to a homogeneous mixture of (ideal) gases. Let us define the **partial**

pressure of a gas in a mixture of gases as the pressure that the gas would exert if it *alone* occupied the entire volume occupied by the mixture. **Dalton's law** states that the pressure exerted by a mixture of gases is the sum of the partial pressures exerted by the components of the mixture. Thus consider a mixture of N gases, occupying a volume V. If j labels the gases, the partial pressure of each satisfies the relation

$$P_j V = n_j RT$$

where n_j is the number of moles of type j in the mixture. By Dalton's law the pressure exerted by the mixture is

$$P = \sum_{j=1}^{N} P_j = \frac{RT}{V} \sum_{j=1}^{N} n_j$$

Therefore, the equation of state for the mixture is the same as that of the pure gas

$$PV = RT \sum_{j=1}^{N} n_j \equiv nRT$$

Let's use Dalton's law of partial pressures to determine the specific gas constant for dry air, which can be modeled as a collection of ideal gases. If the pressure and density of dry are P_d and ρ_d, respectively, then the ideal gas law is given by

$$P_d = \rho_d R_d T$$

where $R_d = R/M_d$. Here M_d is the molar mass of dry air in kilograms (which is also known as the **apparent molecular weight of dry air**). To determine M_d, we note that the analysis of a gas mixture can be expressed in terms of a mole fraction y_i of each component, which is the ratio of the number of moles of a given component to the total number of moles present. According to Avogadro's law, the mole fraction is equal to the volume fraction for ideal gases. Therefore, the apparent molecular weight of any gas mixture (including dry air) is equal to the sum of the mole fraction times the molecular weight of each component. In other words,

$$M_d = \sum_{i=1}^{N} y_i M_i$$

where M_i is the molar mass of each individual gas constituent. Evaluating this for the major constituents of dry air (which is 78% nitrogen, 21% oxygen, and 0.9% argon) gives

$$M_d = \sum_{i=1}^{N} y_i M_i = y_{N_2} M_{N_2} + y_{O_2} M_{O_2} + y_{Ar} M_{Ar}$$

$$= (0.7809)\left(28.02\,\frac{kg}{kmol}\right) + (0.2095)\left(32.00\,\frac{kg}{kmol}\right)$$

$$+ (0.00933)\left(39.94\,\frac{kg}{kmol}\right) = 28.96\,\frac{kg}{kmol}$$

Therefore, for 1 mole of dry air, $M_d = 28.96\ g = 0.02896\ kg$. Thus, the specific gas constant for dry air, is given by

$$R_d = \frac{R}{M_d} = \frac{8.31\ J/mol \cdot K}{0.02896\ kg} \approx 287\ J\ kg^{-1}\ K^{-1}$$

Because Dalton's law applies to air, this implies that the ideal gas equation may be applied to the individual gaseous components of air. For example, the ideal gas equation for water vapor is given by

$$P_v = \rho_v R_v T$$

where R_v is the specific gas constant for water vapor. Repeating the same procedure as above, it can be shown that $M_v = 18.02\ g$, which implies that $R_v \approx 461\ J\ kg^{-1}\ K^{-1}$.

1.4.3 Microscopic Description of an Ideal Gas

In the previous sections, we discussed the macroscopic properties of an ideal gas, including pressure, volume, number of moles, and temperature. In this section we consider the ideal gas model from the microscopic point of view. We will show that the macroscopic properties can be understood on the basis of what is happening on the atomic scale. In addition, we re-examine the ideal gas law in terms of the behavior of the individual molecules that make up the gas. Here, we describe the **kinetic theory of gases**, which gives a remarkably accurate picture of their behavior. The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls. Therefore, we can interpret the pressure and temperature of an ideal gas in terms of microscopic variables.

The model of the kinetic theory of gases makes the following assumptions:

- An ideal gas is made up of molecules, all of which are identical.
- The molecules obey Newton's laws.
- The number of molecules is large, so that the laws of statistics apply.

- Although the number of molecules is large, the volume they occupy is vanishingly small compared to the total volume of the gas
- There are no interactions between the molecules except by hard-body collisions.
- The time during which the molecular collision occur (the collision time) is negligibly small compared with the time spent by the molecules as free particles (free time).
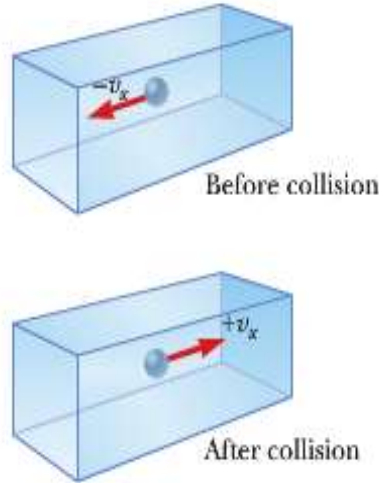
Figure 1.9 A one-dimensional gas molecule moving in a one-dimensional box.

First consider a one-dimensional gas in a one-dimensional box of length L, as shown in Figure 1.9. Let the length of the box lie along the $x -$ axis and consider a single molecule traveling along this axis, for convenience, from left to right. Upon colliding with the wall on the left, the molecule will change direction, moving to the right. If the box is rigid, much heavier than the molecule and if the collision is elastic, the molecule's recoil speed will be the same as its original speed. Its direction is reversed, however, so if v_x is its speed prior to collision, then the change in momentum of the molecule is

$$|\Delta p| = |p_f - p_i| = 2mv_x$$

For the molecule to collide twice with the same wall, it must travel a distance of *2L*. Therefore, the time interval between two collision with the same wall is $\Delta t = 2L/v_x$. Over a time interval that is long compared with Δt, we can estimate the magnitude of average force exerted on the molecule for each collision as

$$|F_{wall}| = \frac{\Delta p}{\Delta t} = \frac{mv_x^2}{L}$$

By Newton's second law, this must be the force exerted by the wall on the molecule and by Newton's third law, it is the force that the molecule exerts upon the wall (in the opposite direction). Therefore, the magnitude of the average force exerted by a single molecule is given by

$$|F_{mol}| = \frac{mv_x^2}{L}$$

If there are N molecules in the box, the rate at which momentum is imparted to the wall, or the total average force on the wall, is

$$\langle F \rangle = \frac{m}{L} \sum_{i=1}^{N} v_{x,i}^2 = \frac{Nm}{L} \langle v_x^2 \rangle$$

where the angular brackets denote that we are speaking about the average behavior. The total pressure on the wall is then just the total average force divided by the cross-sectional area of the wall,

$$P_{total} = \frac{\langle F \rangle}{A} = \frac{Nm}{LA} \langle v_x^2 \rangle \Rightarrow PV = Nm \langle v_x^2 \rangle \quad (1.2)$$

In general, molecules do not travel exclusively in one direction. We expect motion in all directions, randomly distributed between the three linearly independent directions of space. In other words, we expect that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, (where we have used mean square components because the *average* of each component can be expected to vanish since all directions of motion are equally probable). Because

$$v^2 = v_x^2 + v_y^2 + v_z^2 \Rightarrow \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

This implies that

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

We can now write Equation (1.2) as

$$PV = \frac{1}{3} Nm \langle v^2 \rangle$$

Comparing the above expression to the ideal gas law, we find that the temperature is to be associated with the mean kinetic energy

$$kT = \frac{1}{3}m\langle v^2\rangle = \frac{2}{3}\langle K_{mol}\rangle \Rightarrow \langle K_{mol}\rangle = \frac{3}{2}kT \quad (1.3)$$

Equation (1.3) indicates that **temperature is a direct measure of the average molecular translational kinetic energy**. We also obtain an interesting relationship between the root mean square velocity v_{rms} of the gas molecules and the absolute temperature of the gas,

$$v_{rms} \equiv \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$$
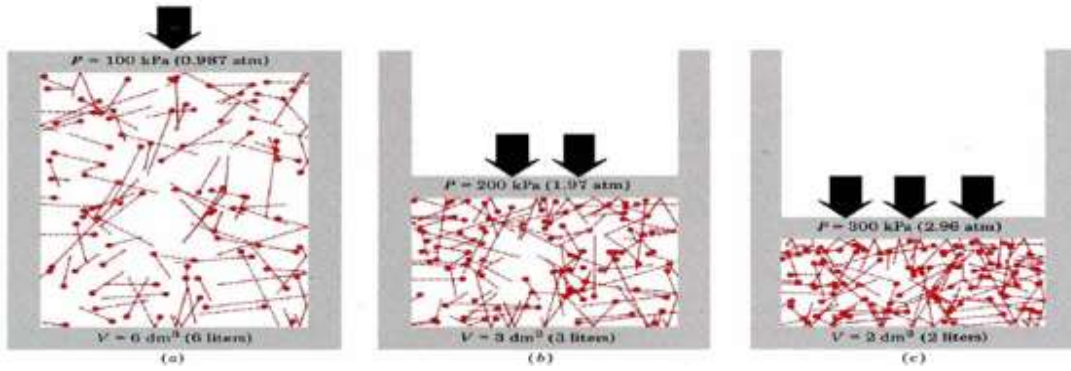
Figure 1.10 Schematic of Boyle's law using kinetic theory.

Returning to Equation (1.2), we can write an expression for the total pressure on the wall as

$$P = \frac{1}{3}\left(\frac{N}{V}\right)m\langle v^2\rangle = \frac{2}{3}n_v\langle K_{mol}\rangle$$

where n_v is the number density of the molecules. This result indicates that **the pressure is proportional to number density and to the average translational kinetic energy of the molecules**. This can be written in terms of the root mean square speed of the molecules as follows:

$$P = \frac{1}{3}n_v m v_{rms}^2 = \frac{1}{3}\rho v_{rms}^2 \quad (1.4)$$

Equation (1.4) gives us a relationship between the pressure of a gas, its density, and the mean molecular speed. Thus, in deriving this simplified model of an ideal gas, we obtain an important result that relates the measurable quantities of pressure and temperature to an atomic quantity –

the average value of the square of the molecular speed. Thus, we have established a key link between the microscopic world and macroscale world. Furthermore, we have connected thermodynamic state variables (pressure and temperature) to basic mechanical quantities (average translational kinetic energy). Hence, in the kinetic theory model, gas molecules act like colliding billiard balls in which the total kinetic energy and linear momentum of the molecules are conserved. In this picture, heat exchange is observed by the exchange of kinetic energy between faster moving molecules and slower moving molecules.

We can also understand the physical basis behind ideal gas law through the kinetic theory model. When a gas is kept at a constant temperature, this implies that average molecular translational kinetic energy also remains constant. Thus, as the volume increases, there are few collisions with the wall of the gas container, leading to a smaller measurable pressure (consistent with Boyle's law). When a gas is kept at a constant pressure, this implies that the average number of collisions per unit time against the gas container must remain constant. Thus, as the volume increases, the only way to maintain the same number of collisions per unit time against the gas container is to increase the total linear momentum of the molecules. This leads to an increase in the average molecular translational kinetic energy, which produces a larger measurable temperature (consistent with Charles' law). When the gas is kept at a constant volume, any increases in the total pressure of the gas will cause an increase in the number of collisions per unit time against the gas container. If the volume is fixed, this must increase the average molecular kinetic energy of the molecules, leading to a higher temperature (consistent with the Guy-Lussac's law). Finally, when the gas is kept at a constant temperature and pressure, then the total energy, momentum, and number density of the gas is fixed. Thus, any increase in the volume of the gas must lead to an increase in the number of moles in the gas in order to keep the number density of the gas constant (consistent with Avogadro's law).

Since we assumed that there were no interactions between the molecules in the assumptions for kinetic theory, the only contribution to the molecular energy comes from the kinetic energy and we have

$$\langle E_{mol} \rangle = \langle K_{mol} \rangle = \frac{3}{2} kT$$

This result essentially states that the total energy associated with point-like molecules is due solely to its translational kinetic energy. Ideal gases that follow this description are called **monatomic ideal gases**. For monatomic ideal gases, we note that

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT \Rightarrow \frac{1}{2} m \langle v_i^2 \rangle = \frac{1}{2} kT$$

where *i* represents *x*, *y*, and *z*. This shows each component contributes an equal amount of energy to the gas, namely $kT/2$. These are called **degrees of freedom** and they refer to the number of

independent means by which a molecule can possess energy. A generalization of this result, which can be derived from statistical mechanics, is called the **equipartition theorem**, which states that **each degree of freedom contributes $kT/2$ to the total energy of a thermodynamic system**. The derivations (and the various implications) of this theorem will be given in a future chapter.
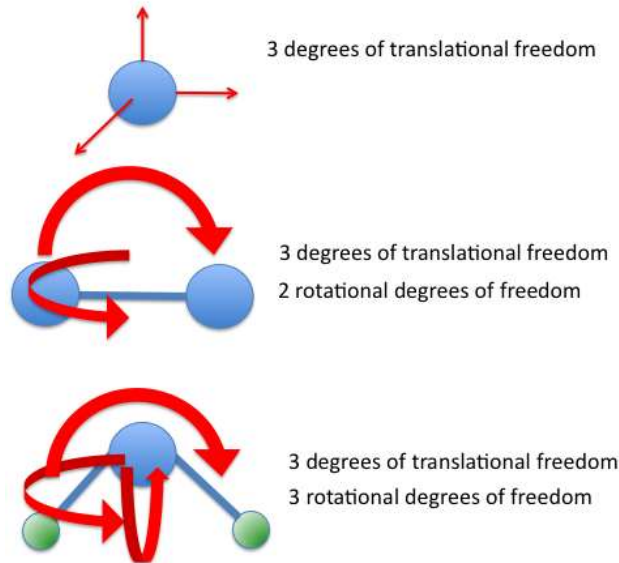
Figure 1.11 Schematic of the degrees of freedom for different molecules

For a monatomic gas (which is composed of point-like molecules), each degree of freedom is associated with the translational kinetic energy of the molecules and thus, monatomic gases have three degrees of freedom. However, different types of molecules will possess more degrees of freedom, as shown in Figure 1.11. For example, diatomic molecules, such as nitrogen and oxygen, possess additional possibilities for energy storage based upon the internal vibration of the molecules and the rotation of the molecules about its center of mass. Thus, diatomic molecules will have six degrees of freedom (3 degrees associated with translations, 2 degrees associated with rotation, and 1 degree associated with vibration). This leads to a total energy of $3kT$ for the diatomic molecules. In general, it can be shown that for polyatomic molecules of an ideal gas, the total energy associated with the molecules is

$$\langle E_{mol} \rangle = \frac{f}{2} kT$$

where f is the number of degrees of freedom per molecule.

1.4.4 Boltzmann Distribution Law
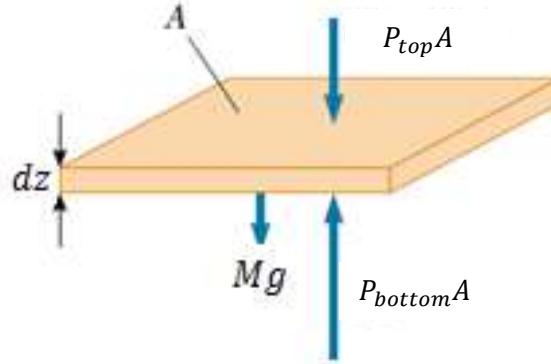
Figure 1.8 An atmospheric layer of thickness dz and cross-sectional area A at rest.

The ideal gas law also helps us to determine how the distribution of molecules in our atmosphere. In particular, let's determine how the number density of molecules varies with altitude. Our model assumes that the atmosphere is at a constant temperature. Let's consider an atmospheric layer of thickness dz and cross-sectional area A at rest. Because the air is in static equilibrium, the forces operating on the slab must be balanced. Thus, the magnitude of the upward force, $F_{up} = P_{bottom}A$, exerted on the bottom of this layer must be balanced with the magnitude of the downward force on the top of the layer, $P_{top}A$, and the weight of the gas in this thin layer, Mg. Using Newton's 2nd law, we have

$$F_{net} = P_{bottom}A - P_{top}A - Mg = 0 \Rightarrow \left(P_{bottom} - P_{top}\right)A = \rho Vg \Rightarrow \frac{dP}{dz} = -\rho g \quad (1.5)$$

Equation (1.5) is known as the **hydrostatic equation** and it expresses a fundamental balance between the gravitational force and the vertical pressure gradient force in the atmosphere.

Using the ideal gas law, the density can be written as

$$\rho = \frac{M}{V} = \frac{\langle m \rangle N}{V} = \frac{\langle m \rangle P}{kT}$$

where $\langle m \rangle$ is the average mass of air molecule. Therefore, the hydrostatic equation becomes

$$\frac{dP}{dz} = -\rho g = -\frac{\langle m \rangle P}{kT}g$$

This expression is known as the **barometric equation** and it applies for any ideal gas. Since T is constant, we can solve this differential equation to obtain

$$\frac{dP}{P} = -\frac{\langle m \rangle}{kT} g \, dz \Rightarrow P(z) = P_0 \exp\left[-\frac{\langle m \rangle g z}{kT}\right] \quad (1.6)$$

According to the ideal gas law, we can write the pressure as

$$P = n_v kT$$

where $n_v = N/V$ is the number density of the molecules. Since the pressure is proportional to the number density (at constant temperature), this implies that the number density must also have the same form as equation (1.3). This gives us an expression known as the **law of atmospheres**

$$n_v(z) = n_v(0) \exp\left[-\frac{\langle m \rangle g z}{kT}\right] \quad (1.7)$$

According to Equation (1.7), the number density decreases exponentially with altitude when the temperature is constant. A comparison of this model with the actual atmospheric pressure as a function of altitude shows that the exponential form is a reasonable approximation to Earth's atmosphere.

The exponential function that appears in Equation (1.7) can be interpreted as a probability distribution that gives the relative probability of finding a gas molecule at some height z. Thus, the probability of find a gas molecule at some height z must be proportional to the number density distribution $n_v(z)$. This concept enables us to determine many properties of the atmosphere, such as the fraction of molecules below a certain height or the average potential energy of a molecule. Because the gravitational potential energy of a molecule at height z above Earth's surface is $U = mgz$, we can express the law of atmospheres as

$$n_v(U) = n_v(0) \exp\left[-\frac{U}{kT}\right]$$

This expression means that gas molecules in thermal equilibrium are distributed in space with a probability that depends on their gravitational potential energy. This exponential expression describing the distribution of molecules in the atmosphere is powerful and applies to any type of energy. In general, the number density of molecules having energy E is

$$n_v(E) = n_v(0) \exp\left[-\frac{E}{kT}\right]$$

This equation is known as the **Boltzmann distribution law** and it is important in describing the statistical mechanics of a large number of molecules. It states that **the probability of finding the molecules in a particular energy state varies exponentially with energy**. All the molecules would fall into the lowest energy if the thermal agitation at a temperature T did not excite the molecules to higher energy levels.

Now that we have described the fundamental relationships between the basic state variables (pressure, volume, and temperature), the next couple of chapters will examine the laws of thermodynamics. In the next chapter, we will examine the first law of thermodynamics.

Chapter 2: The 1st Law of Thermodynamics

       Until about 1850, the fields of thermodynamics and mechanics were considered two distinct branches of science, and the law of conservation of energy seemed to describe only certain kinds of mechanical systems. However, mid-19th century experiments performed by James Joule and others showed that energy may be added to (or removed from) a system either by heat or by doing work on the system (or having the system do work). Today, we know that internal energy (which we formally define in this chapter), can be transformed to mechanical energy. Once the concept of energy was broadened to include internal energy, the law of conservation of energy emerged as a universal law of nature. This chapter focuses on the concept of internal energy, the first law of thermodynamics, and some of the important applications of the first law. The first law of thermodynamics is essentially a law of conservation of energy for macroscopic systems. Conservation can be imposed by requiring that the variation of the total energy of the system and its environment is identically zero. However, in order to make this precise, one should be able to say what exactly the energy of a macroscopic system is in the first place. We begin with the definition of the internal energy.

2.1 Internal Energy

       Since every macroscopic system can be decomposed into a large number of elementary constituents, every macroscopic system is eventually a mechanical system, and thus it is reasonable to say that its energy is just the average total mechanical energy, i.e., the sum of the kinetic and potential energies of its constituents. Thus, the **internal energy** is all the energy of a system associated with its elementary constituents when viewed from a reference frame at rest with respect to the object. The last part of the sentence above ensures that any bulk kinetic energy of the system due to its motion in space is not included in internal energy. Internal energy includes translational kinetic energy; rotation and vibration of molecules; potential energy within molecules; and potential energy between molecules.

       It's important that we make a major distinction between internal energy and heat. Whereas internal energy is the *total energy* of a given thermodynamic system, heat is defined as the *transfer of energy* across the boundary of a system due to a temperature difference between the system and its surroundings. Furthermore, whereas the heat exchanged between a system and its surroundings depends on the actual thermodynamic process (and thus, the path taken in thermodynamic phase space), the internal energy is *independent* of the thermodynamic process and thus depends only upon the end points in thermodynamic phase space. For this reason, we

call the internal energy a **state function** and thus $U = U(\vec{Z})$, where $\vec{Z}$ is used to denote all the state variables of a given system (such as temperature, pressure, volume, composition, etc).

Elementary kinetic theory from the previous chapter describes that the internal energy of an ideal gas is just the sum of the individual molecular kinetic energies

$$U = N\langle E_{mol}\rangle = \frac{f}{2}NkT$$

This implies that **the internal energy of an ideal gas is a function only of the absolute temperature**. This result was also verified experimentally by James Joule. Consider two isolated chambers A and B are joined by a tube with a stop-cock separating them, as shown in Figure 2.1. Chamber A is filled with an ideal gas up to a certain pressure whereas chamber B is a vacuum. The stop-cock is suddenly opened so that the gas flows freely from A to B. In doing so the gas does no work, so $dU = 0$. Now the final temperature, volume, and pressure of the gas are measured and it is found that $dT = 0$. Since $dP \neq 0$ and $dV \neq 0$, we must conclude that $U = U(T)$ for an ideal gas.
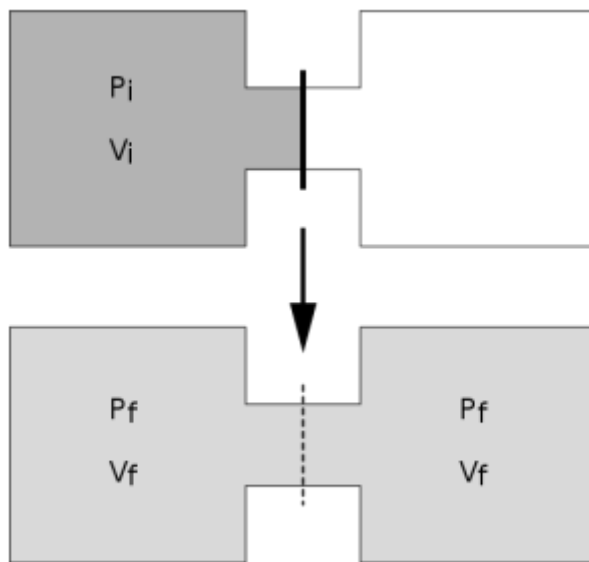
Figure 2.1 Schematic of the Joule free expansion experiment

As mentioned in the introduction, the first law of thermodynamics is essentially a law of conservation of energy for macroscopic systems. However, for a particular system, there are two ways in which the internal energy can change: energy transfer caused by temperature gradients across the system boundary (i.e. heat) and energy transfer caused by changes in the external parameters of the system (i.e. work). Thus, we will be concerned with energy conservation in thermodynamic processes, which involves the work done by a thermodynamic system on the

environment and the heat exchanged between a thermodynamic system and its environment. In the following subsections, we will define work and heat for thermodynamic processes.

2.1.1 Work
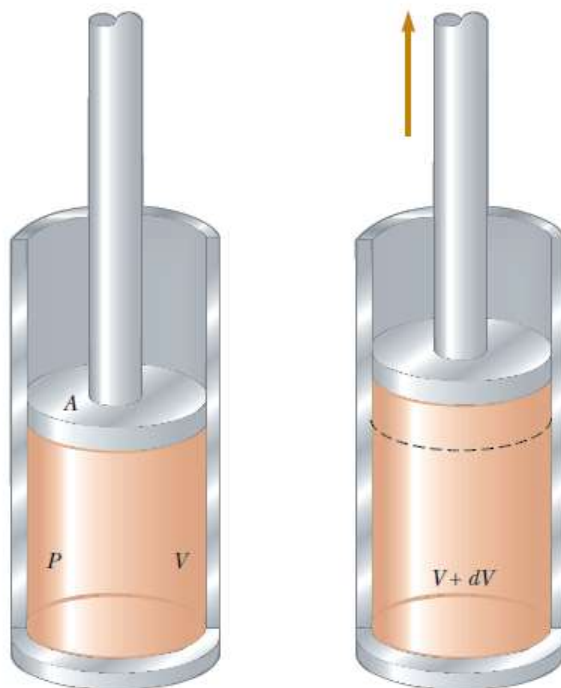
Figure 2.2 Work done by a gas contained within a piston

To give a mathematical description of the work done by a gas contained within a piston, let S be the (closed) boundary of our system and let $\vec{F}_n$ be the net force exerted by the system on an infinitesimal surface element $d\vec{S}$ of the boundary. Suppose that the boundary experiences a deformation, so that the infinitesimal area $d\vec{S}$ is displaced by $d\vec{r}$. The infinitesimal work done by the system on the boundary is then

$$\delta W = \vec{F}_n \cdot d\vec{r} = P\left(d\vec{S} \cdot d\vec{r}\right)$$

Now the quantity $d\vec{S} \cdot d\vec{r}$ may be interpreted as the infinitesimal contribution to the change in volume dV of the closed surface S by the displacement of $d\vec{S}$ along $d\vec{r}$, as shown in Figure 2.2. Therefore, the work done by the system on the environment in changing its volume by dV is given by

$$\delta W = -P \, dV$$

δW is called an **inexact differential** because its integral depends on the path that is taken in the phase space of the system as it goes from its initial state to its final state. In other words, the integral of δW depends on the thermodynamic process.

In general, the infinitesimal work done by a thermodynamic system will have the form

$$\delta W = \sum_i P_{X_i} dX_i$$

where X_i are some external parameters (different from the energy) which governing the system and P_{X_i} are the **generalized forces** associated with their deformation. The generalized force P_{X_i} is said to be **conjugate** to the external parameter X_i. Pressure in a fluid is just one example of a generalized force in thermodynamics, being the generalized force conjugate to the volume. However, there are other generalized forces that can operate in a thermodynamic system. For example, one can show that the work done by the surface tension, σ, during an interfacial expansion is

$$\delta W = \sigma dA$$

In some cases (such as during nucleation of cloud droplets), this may actually be the major contribution to the work done – more important than the $P \, dV$ term. Other examples of mechanical work are the work done by friction, $\vec{f}$,

$$\delta W = f \, ds$$

where ds is an infinitesimal displacement tangent to the path of the body and the work done by the tension, $\vec{\tau}$, in a wire of length L in elongating it by dL is

$$\delta W = \tau dL$$

We will discuss more about generalized forces during our discussion on thermodynamic potentials.

2.1.2 Heat

Heat is energy transferred into or removed from a macroscopic system on the molecular level, as opposed to the direct application of mechanical work on the system by deformations of

its macroscopic parameters. While the transfer of energy may occur because of an existing difference in temperatures between two macroscopic systems, this is not the only way in which the transfer may occur. For example, friction transfers energy from a mechanical system into its environment. A block sliding along the rough surface of a table transfers mechanical energy to the table although no work is done on the table. Stirring liquid in a cup or shaking it in a flask transfers mechanical energy from the stirring or shaking device to the liquid, as evidence by the rise in temperature of the liquid. Again, no work is done on the liquid since its volume remains unchanged. In both cases, the energy is transferred by heat.

This understanding of the relationship between heat and energy is relatively modern. It was Sir Benjamin Thompson (Count Rumford) who, while supervising the manufacture of canons for the government of Bavaria, noticed that the more the canons were bored the more the water that was required to cool them. Noticing that the supply of "heat" from boring a canon was inexhaustible and that no chemical change had actually occurred in the material of the bored canon, he associated heat with the mechanical energy that went into the boring process. Nearly fifty years later Helmholtz declared that heat is a form of energy and that all forms of energy are equivalent and interchangeable. However, while one form of energy can be exchanged for another or transferred from one subset of the universe to another, energy itself cannot be created nor destroyed and the total amount of energy present within the universe is constant.
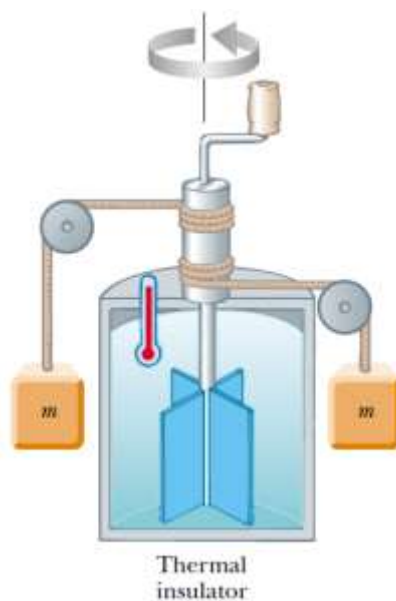
Figure 2.3 Joule's paddlewheel experiment for determining the mechanical equivalence of heat. The falling blocks rotate the paddles, causing the temperature of the water to increase.

Although the connection between mechanical and internal energy was first suggested by Benjamin Thompson, it was Joule who established the equivalence of these two forms of energy. A schematic of Joule's most famous experiment is shown in Figure 2.3. The system of interest is the water in a thermally insulated container. Work is done on the water by a rotating paddle

wheel, which is driven by heavy blocks falling at a constant speed. The stirred water is warmed due to the friction between it and the paddles. If the energy lost in the bearings and through the walls is neglected, then the loss in potential energy associated with the blocks equals the work done by the paddle wheel on the water. If the two blocks fall through a distance h, the loss in potential energy is $2mgh$, where m is the mas of one block; it is this energy that causes the temperature of the water to increase. By varying the conditions of the experiment, Joule found that the loss in mechanical energy $2mgh$ is proportional to the increase in water temperature ΔT. The proportionality constant was found to be approximately $4.18\,J/g°C$. Hence, 4.18 J of mechanical energy raises the temperature of 1 gram of water by 1°C. More precise measurements taken later demonstrated the proportionality to be $4.186\,J/g°C$ when the temperature of the water was raised from $14.5°C$ to $15.5°C$. We adopt this "15-degree calorie" value: 1 cal $\equiv$ 4.186 J. This equality is known, for purely historical reasons, as the **mechanical equivalent of heat.** For a historical perspective on the Joule paddlewheel experiment, see the following article:

https://www.aps.org/publications/apsnews/200912/physicshistory.cfm

2.2 The First Law of Thermodynamics

Suppose that a thermodynamic system is isolated in such a way that it exchanges no energy with its environment. Therefore, the system is transformed from some initial state, i, to some final state, f, and thus $U(\vec{Z_i}) = U(\vec{Z_f})$. If some external forces are acting upon the system by virtue of its interaction with the environment then there is no reason to assume that the internal energy would stay constant. Our system may do work upon the environment or have work done upon it by the environment via the external forces, in which case one may argue that the change in internal energy should be equal to the work done,

$$dU(\vec{Z}) = \delta W = -\sum_i P_{X_i}\, dX_i \quad (2.1)$$

where P_{X_i} is the "pressure" associated with the deformation of the external parameters X_i of the system. We have chosen our sign conventions in such a way that work would be negative when the system does work and positive when work is done upon it.
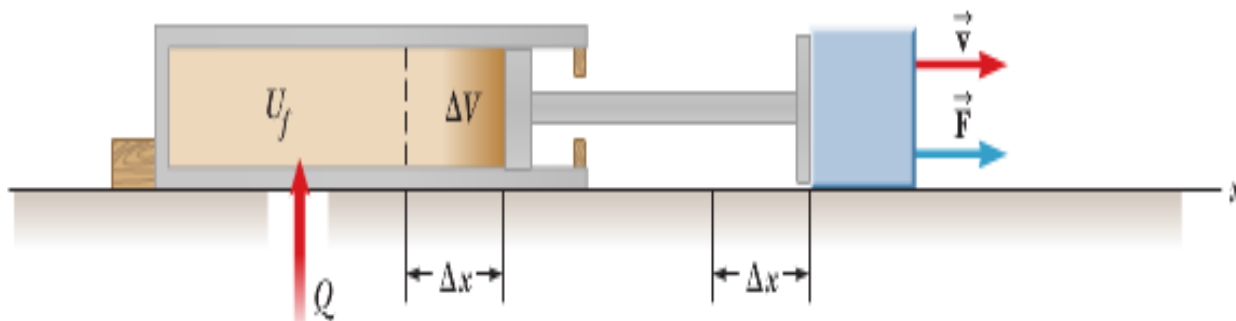
Figure 2.4 Schematic of the first law of thermodynamics

Equation (2.1) would hold true *only* if the work done were independent of the actual transformation process in going from the initial state, *i*, to the final state, *f*, because we have assumed that the internal energy is a function of the state variables and so the left hand side of Equation (2.1) is an exact differential. However, we have already noted that the right hand side, δW, is not an exact differential, so we can expect that the change in internal energy will *not* always be the work done by the system. For example, when an ideal gas is compressed at constant temperature, work is done on the gas but its internal energy remains unchanged. Situations like this would mean one of two things: either energy is not conserved or the system is able to exchange energy with its environment in a form that is different from mechanical work. If we assume that energy is conserved, then we must include a new quantity δQ, which would represent the energy transferred by any means *other* than by mechanical work,

$$dU = \delta W + \delta Q$$

The inexact differential δQ is the heat. It cannot be an exact differential because δW is not an exact differential, but the sum of δQ and δW must be an exact differential. We have thus arrived **first law of thermodynamics**, which states that there is a function of state, called the internal energy, which satisfies the following relationship

$$dU = \delta Q + \delta W$$

The first law states that there are two ways in which the internal energy of a system can change: by doing work (which requires a macroscopic displacement of an object through the application of a force), and by a direct exchange of energy across the system boundary as heat (which requires a temperature difference between a system and its environment). The first law also implies that both work and heat transfer energy across a system's boundary. Any energy δQ exchanged between the system and the environment and any work done through the expansion or compression of the system results in a change in the internal energy, dU, of the system, as shown in Figure 2.4. Since U is a state variable, a change in internal energy results in measurable changes in the macroscopic variables of the system (such as temperature).

37

Let's pause to reiterate the sign conventions being used here. $\delta Q > 0$ implies that energy is transferred *into* the system via heat, whereas $\delta Q < 0$ implies that energy is released by the system into the environment via heat. $\delta W > 0$ implies that work is done on the system by the environment, $\delta W < 0$ implies that work is done by the system on the environment.

2.3 Response Functions

The first law of thermodynamics guarantees that when work is done on the system and/or heat is added/removed from a system, there will be a change in the internal energy of the system. A basic question can be raised: do all thermodynamic systems respond in the same manner to work and heat? In other words, do all substance respond in the same way to heat transfer and energy transfer via work? The general answer to this question is no and in the next section, we will examine the mechanical and caloric response functions.

2.3.1 Specific Heat

Back when heat was considered a fluid (called caloric) a unit of heat was defined as the amount of heat required to raise the temperature of one gram of pure water at standard pressure from 14.5 to 15.5 degrees Celsius. This unit was defined as the **calorie**. Notice that it is necessary to specify the material, its mass, and the temperature range in order to have a precise definition of the calorie. This is because of the well-known experimental fact that the amount of heat required to raise the temperature of a substance by one degree Kelvin depends on all of these factors. We define the **heat capacity** of a thermodynamic system as the amount of heat required to raise the temperature of the system by one degree kelvin

$$C = \frac{\delta Q}{\delta T}$$

where δQ is the heat absorbed and δT is the change in temperature, and it is measured in cal/°C. Notice that δQ is an inexact differential because it depends on the process by which energy is transferred. We also know from common experience that the heat capacity C depends on the composition of the system and its mass. We can eliminate its dependence on the mass of the system by defining the **specific heat** as

$$c = \frac{1}{m}\frac{\delta Q}{\delta T}$$

where m is the system's mass. The specific heat of a substance is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to cause a particular

temperature change. In other words, specific heats are a measure of the response of a substance to heat transfer. One calorie can be thought of as the specific heat of pure water at standard pressure, so the specific heat of pure water is 1 cal/g°C.

TABLE 20.1	Specific Heats of Some Substances at 25°C and Atmospheric Pressure	
	Specific Heat c	
Substance	**J/kg · °C**	**cal/g · °C**
Elemental Solids		
Aluminum	900	0.215
Beryllium	1 830	0.436
Cadmium	230	0.055
Copper	387	0.092 4
Germanium	322	0.077
Gold	129	0.030 8
Iron	448	0.107
Lead	128	0.030 5
Silicon	703	0.168
Silver	234	0.056
Other Solids		
Brass	380	0.092
Glass	837	0.200
Ice (−5°C)	2 090	0.50
Marble	860	0.21
Wood	1 700	0.41
Liquids		
Alcohol (ethyl)	2 400	0.58
Mercury	140	0.033
Water (15°C)	4 186	1.00
Gas		
Steam (100°C)	2 010	0.48

Figure 2.5 A table of the specific heats for common substances from *Physics for Scientists and Engineers* by Serway and Beichner.

Now generally, for a given composition and a given process, the heat capacity will also be a function of the temperature. In terms of the specific heat,

$$c = \frac{1}{m}\frac{\delta Q}{\delta T} \Rightarrow \Delta Q = m \int_{T_i}^{T_f} c(T)\, dT$$

For many substances and processes of interest, $c(T)$ is a slowly varying function of the temperature and as long as temperature does not change too much it is a good approximation to replace $c(T)$ by c_{av}. Therefore, if it is known that $c(T)$ is approximately constant during the process of heating, then

$$\Delta Q \approx mc(T_f - T_i)$$

Because δQ is an inexact differential, this necessarily implies that heat capacity will depend upon the thermodynamic process. Two heat capacities are of interest: (i) the heat capacity at constant volume C_V and (ii) the heat capacity at constant pressure C_P. It's easy to see then that

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P$$

If we restrict our attention to ideal gases, we can write

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow \Delta U = \int_{T_i}^{T_f} C_V(T) \, dT$$

where C_V is a function of temperature only. The first law takes the form

$$\delta Q = C_V \, dT + P \, dV$$

for *all* processes of an ideal gas. Elementary kinetic theory indicates that the internal energy of an ideal gas is a function of temperature only: $U(T) = (f/2) NkT$. Therefore, it also immediately follows that the heat capacity of the gas at constant volume is,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2} Nk$$

and the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P = \frac{f}{2} Nk + P \left(\frac{Nk}{P}\right) = \left(\frac{f}{2} + 1\right) Nk$$

Thus, the difference between the heat capacities is $C_P - C_V = Nk$. This implies that $C_P > C_V$ for an ideal gas. In contrast to C_V, C_P includes the effect of work on increasing the temperature of any given substance. In order to increase the temperature of any substance (and thus to increase the substance's internal energy), more heat must be added in order to compensate for the energy lost due to work done on the environment.

These results also give us a way to determine the degrees of freedom of a gas and a test for the equipartition theorem. For a monotonic gas like helium, we expect that the heat capacity per mole is

$$C_V = \frac{3}{2}Nk = \frac{3}{2}nR \Rightarrow \frac{C_V}{n} = \frac{3}{2}R = 12.5\frac{J}{K}$$

For diatomic and polyatomic molecules, the heat capacity should be larger, in proportional to the number of degrees of freedom per molecule. For a solid, there are six degrees of freedom per atom so the heat capacity per mole is

$$\frac{C_V}{n} = \frac{6}{2}R = 3R = 25.0\frac{J}{K}$$

This general result is called the **rule of Dulong and Petit.**

Figure 2.6 shows a plot of C_V as a function of temperature for one mole of hydrogen gas. Below about 100 K, $C_V \approx 1.5\ nR$, which implies that only three translational degrees of freedom are active. In other words, there is a temperature threshold before rotational kinetic energy becomes important. Around room temperature the two rotational degrees of freedom are active, and around 1000 K, the two vibrational degrees of freedom also become active.
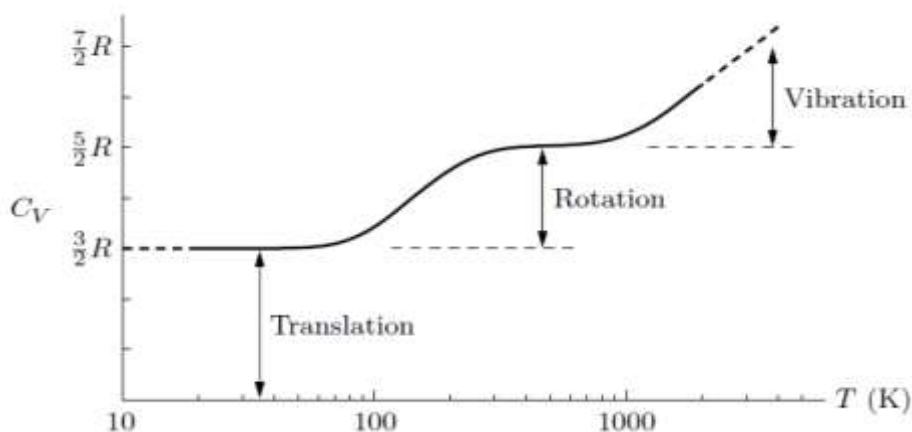
Figure 2.6 Heat capacity at constant volume of one mole of hydrogen gas. Note that the temperature is logarithmic. Copyright ©2000, Addison-Wesley.

Figure 2.7 plots measured values of C_P for one mole each of lead, diamond, and aluminum and the solid curves show the theoretical values for C_V for each substance. At sufficiently high temperatures, C_V for each material approaches the value $3R$ predicted by the law of Petit and Dulong. This indicates that the equipartition theorem is valid only for solids at sufficiently high temperatures (a result that will proved in future chapters). Furthermore, the discrepancies between the data and the solid curves at high temperatures are mostly due to the differences between C_P and C_V. However, as the temperature decreases, C_P and C_V begin to converge together. At $T = 0$, both C_P and C_V go to zero, indicated that there are zero degrees of freedom for the system as the solids approach absolute zero.
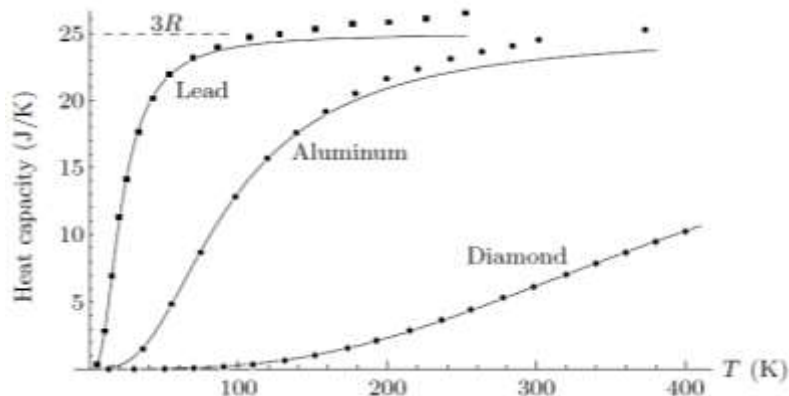
Figure 2.8 Measured heat capacities at constant pressure (data points) for one mole each of three different elemental solids. The solid curves show the heat capacity at constant predict by the model used in Section 7.5 in *Thermal Physics* by Schroeder, with the horizontal data chosen to best fit the data. Copyright ©2000, Addison-Wesley.

2.3.2 Latent Heat

The heat capacity of a system is a useful concept so long as the process involves a temperature change. Yet, energy may be absorbed or released from a system during constant temperature processes as well. In a class of such processes, a substance changes phase, say from solid to liquid and vice-versa or liquid to gas and vice-versa or from solid to gas and vice-versa. Such processes are referred to as **phase transitions**. During phase transitions, the temperature of the substance remains constant but energy must continue to be transferred either into or out of the system for the process to continue. For example, if the source of energy (such as a stove) is turned off during the boiling of water the process ceases. This shows that heat is required to be absorbed by the water in order to maintain the boiling, yet the temperature of the water itself remains constant throughout. The energy that is being absorbed by the water is required to convert the liquid into vapor.

We define the **latent heat** as the heat required to change the phase of one gram of a substance,

$$L = \frac{\Delta Q}{m}$$

and is measured in cal/g. The latent heat is associated with a particular kind of phase transition and a particular substance. As you might expect, different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangement vary. Also, the amount of energy transferred during a phase change depends on the amount of substance involved (i.e. it takes less energy to melt an ice cube that it does to thaw a frozen lake).

42

The value of the latent heat for a substance depends on the nature of the phase change, as well as on the properties of the substance. The **latent heat of fusion L_f** is the term used when the phase change is from solid to liquid and the **latent heat of vaporization L_v** is the term used when the phase change is from liquid to gas. The latent heat of various substances vary considerably, as Figure 2.9 shows. For example, the latent heat of the vaporization of water $L_v = 2.26 \times 10^6 \, J/kg = 540 \, cal/g$, i.e., it takes 540 calories of heat to vaporize one gram of water. When the vapor condenses, every gram will then release 540 calories. Similarly, the heat released from water when one gram freezes to form one gram of ice at standard pressure is 80 calories, i.e, the latent heat of fusion is $L_f = 80 \, cal/g = 3.33 \times 10^5 \, J/kg$. When ice melts at standard pressure, it absorbs 80 cal/g.

TABLE 20.2 Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	−269.65	5.23×10^3	−268.93	2.09×10^4
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

Figure 2.9 A table of the latent heats for common substances from *Physics for Scientists and Engineers* by Serway and Beichner.

Heat capacities, specific heats and latent heats of substances are measured using **calorimetry**. Generally speaking a calorimetric experiment involves the transfer of energy between two or more thermodynamic systems while the combination of the systems is kept isolated from the rest of the universe. Devices in which the exchange of energy occurs are called **calorimeters**, whose main function is to isolate whatever is placed inside. Since the combination of thermodynamic systems is kept isolated, the calorimetric process satisfies $\Delta Q = 0$, where ΔQ represents the energy exchanged by the combination with the rest of the universe. Denoting the systems by the subscript j, this means that

$$\Delta Q = \sum_j \Delta Q_j$$

where ΔQ_j is the energy absorbed (positive) or liberated (negative) by system j.
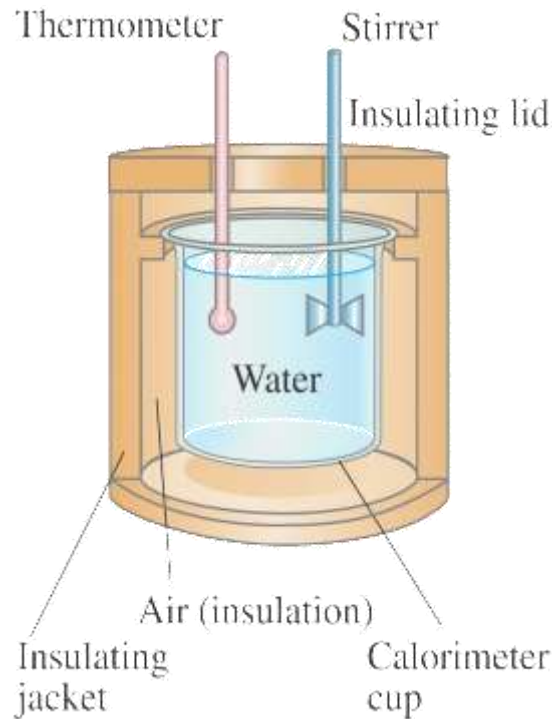
Figure 2.10 Schematic of a typical calorimeter

Example: A copper block of mass 75 g is taken from an oven and placed in a glass of 300 g which contains 200 g of water. Assume that the initial temperature of the glass and water is 12^0C and the temperature of the oven is 500^0C. If the temperature of the glass and water rises to 24.7^0C, determine the specific heat of copper.

Answer: Let's assume that no energy is lost to the environment and that there is no vaporization of the water during the process. Therefore, energy is only exchanged between the copper block, the glass, and the water. Furthermore, let's assume that the specific heats of the glass, copper, and water are independent of temperature. We have

$$Q_{TOTAL} = \Delta Q_c + \Delta Q_g + \Delta Q_w = 0$$
$$\Rightarrow m_c c_c (T_f - T_{i,c}) + m_g c_g (T_f - T_{i,g}) + m_w c_w (T_f - T_{i,w}) = 0$$

Solving for c_c gives

$$c_c = -\frac{m_g c_g (T_f - T_{i,g}) + m_w c_w (T_f - T_{i,w})}{m_c (T_f - T_{i,c})} = 0.0926 \frac{cal}{g\ °C} = 388 \frac{J}{kg\ °C}$$

2.3.3 Thermal Expansion

Our discussion of the liquid thermometer in the previous chapter made use of one of the best-known changes in a substance: As its temperature increases, its volume almost always increases. This phenomenon, known as **thermal expansion**, has an important role in numerous engineering applications (such as the use of thermal expansion joins in buildings, concrete highways, railroad tracks, brick walls, and buildings).

Thermal expansion is a consequence of the change in the average separation between the constituent atoms in an object. To understand this, we can use a mechanical model of the atomic configuration of a substance, in which the atoms (which can be modeled as spheres) are imagined to be attached to each other by springs which reflect the elastic nature of the interatomic forces, as shown in Figure 2.11. At ordinary temperatures, the atoms in a solid oscillate about their equilibrium positions with an amplitude of approximately $10^{-11}\ m$ and a frequency of approximately $10^{13}\ Hz$. The average spacing between the atoms is about $10^{-10}\ m$. As the temperature of the solid increases, the atoms oscillate with greater amplitudes; as a result, the average separation between them increases. Consequently, the object expands.
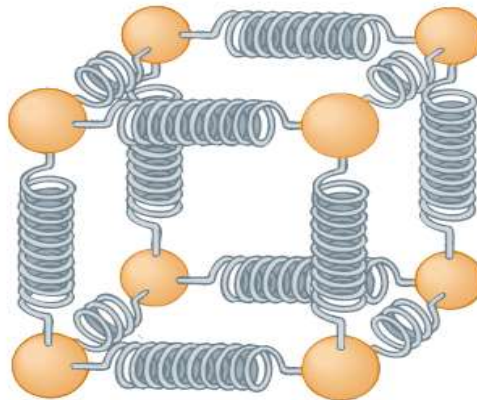
Figure 2.11 A mechanical model of the atomic configuration in a substance

It is a matter of common experience that the amount of thermal expansion varies for many substances, and in some substances the volume decreases when the temperature increases. If thermal expansion is sufficiently small relative to an object's initial dimensions, the change in any dimension is, to a good approximation, proportional to ΔT. Suppose that an object has an initial length L_i along some direction at some temperature and that the length increases by an amount ΔL for a change in temperature ΔT. Because it is convenient to consider the fractional change in length per degree of temperature change, we define the **average coefficient of linear expansion as**

$$\bar{\alpha} \equiv \frac{\Delta L / L_i}{\Delta T}$$

Experiments show that α is constant for small changes in temperatures, which implies that $\Delta L = \alpha L_i \Delta T$. For large changes in temperature, α is no longer constant and can be defined as

$$\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P$$

Because the linear dimensions of an object change with temperature, it follows that surface area and volume change as well. The change in volume (at constant pressure) is proportional to the initial volume V_i and to the change in temperature according to relationship. $\Delta V = \bar{\beta} V_i \Delta T$ where $\bar{\beta}$ is the **average coefficient of volume expansion**. For a solid, the average coefficient of volume expansion is approximately three times the average linear expansion coefficient: $\bar{\beta} = 3\bar{\alpha}$ (this assumes that the average coefficient of linear expansion of the solid is the same in all directions). Experiments show that β is constant for small changes in temperatures, but for large changes in temperature, β is no longer constant and can be defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

TABLE 19.2 Average Expansion Coefficients for Some Materials Near Room Temperature

Material	Average Linear Expansion Coefficient (α) $(°C)^{-1}$	Material	Average Volume Expansion Coefficient (β) $(°C)^{-1}$
Aluminum	24×10^{-6}	Alcohol, ethyl	1.12×10^{-4}
Brass and bronze	19×10^{-6}	Benzene	1.24×10^{-4}
Copper	17×10^{-6}	Acetone	1.5×10^{-4}
Glass (ordinary)	9×10^{-6}	Glycerin	4.85×10^{-4}
Glass (Pyrex)	3.2×10^{-6}	Mercury	1.82×10^{-4}
Lead	29×10^{-6}	Turpentine	9.0×10^{-4}
Steel	11×10^{-6}	Gasoline	9.6×10^{-4}
Invar (Ni–Fe alloy)	0.9×10^{-6}	Air at 0°C	3.67×10^{-3}
Concrete	12×10^{-6}	Helium	3.665×10^{-3}

Figure 2.12 A table of expansion coefficients for typical substances from *Physics for Scientists and Engineers* from Serway and Beichner

Figure 2.12 lists the average coefficient of linear expansion for various materials. Note that for these materials, α is positive, indicating an increase in length with increasing temperature. This is not always the case. Some substances—calcite (CaCO3) is one example—expand along one dimension (positive α) and contract along another (negative α) as their temperatures are increased.

2.3.4 Compressibility

When work is usually done on a substance, it will usually result in a change in the volume. A measure of the fractional volume change is known as **isothermal compressibility**, which is defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Mathematically, κ_T is the fractional decrease in volume per infinitesimal change in pressure. Hence, κ_T is a measure of the relative volume change of a fluid or solid as a response to a pressure change. In other words, κ_T is a parameter that determines how a substance responds to changes in pressure if the temperature remains constant.

Another measure of the fractional volume change when work is done on a substance is known as the **bulk modulus**.

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T = \kappa_T^{-1}$$

Mathematically, B is the ratio of the infinitesimal pressure increase to the resulting *relative* decrease of the volume. The bulk modulus characterizes the response (or resistance) of a substance to uniform squeezing or to a reduction in pressure.

The compressibility of a gas has numerous applications in fluid dynamics. One application involves the speed of sound in a gas. The speed of sound in a gas depends on the "springiness" of the gas. That is, it depends on how the volume of the gas responds to changes in pressure. Sir Isaac Newton assumed that the speed of sound was an isothermal process and used the isothermal compressibility to calculate the speed of sound in a gas. His answer did not agree with experiment. It turns out that sound waves cause oscillations in pressure but the oscillations are fast enough that heat cannot move from compressed regions to rarified regions in order to keep the temperature constant. Before the heat can be conducted away from the compressed regions the compression has moved on. Therefore, another compressibility parameter is needed to describe how a substance responds to changes in pressure if no heat is exchanged between the system and the environment. This parameter is known as the **adiabatic compressibility** or the **isentropic compressibility**

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

We will discuss this parameter in more detail in future chapters.

2.4 Heat Transfer Mechanisms

It is important to understand the rate at which energy is transferred between a system and its surroundings and the mechanisms responsible for the transfer. Therefore, let us now look at three common energy transfer mechanisms that can result in a change in internal energy of a system.

2.4.1 Conduction

Energy transfer between two macroscopic systems due to a difference in temperature between them and which does not involve the gross movement of matter is called **conduction**. This process bears primary responsibility for energy transfer in solids. Conduction can be understood on the microscopic scale as the direct exchange of mechanical energy from a region of higher temperature to a region of lower temperature by molecular collisions at the boundary, *without* recourse to the bulk motion of the substance. It is most effective in solids and can occur in liquids but not in gases because of their low molecular density, which implies that molecular collisions simply do not occur frequently enough.
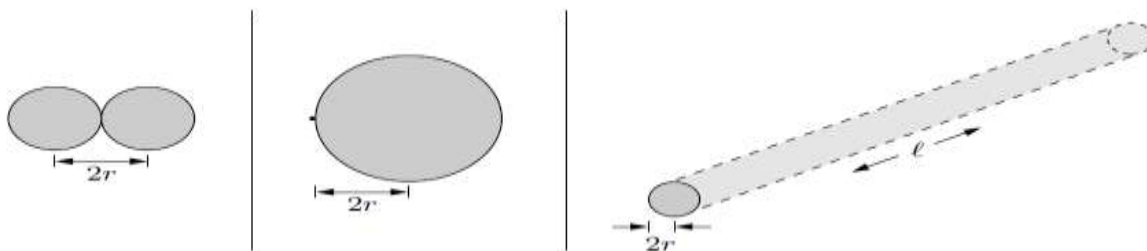
Figure 2.13 A schematic of the mean free path of a molecule. Copyright © 2000, Addison Wesley.

The rate of heat conduction is governed by the **mean free path**, which is a measure of how far a molecule can travel before collisions. We can approximate the mean free path using kinetic theory. If molecules have diameter d, then the effective cross-section area for the collision is given by $A = \pi d^2$, using a circle of diameter $2d$ to represent a molecule's effective collision area while treating the target molecules as point masses as shown in Figure 2.13. In time t, the circle would sweep out the volume $\pi d^2 \langle v \rangle t$ and the number of collisions can be estimated from the number of gas molecules that were in that volume. Thus, the mean free path could then be taken as the length of the path divided by the number of collisions.

$$l \approx \frac{\langle v \rangle t}{\pi d^2 \langle v \rangle t n_v} = \frac{1}{\pi d^2 n_v}$$
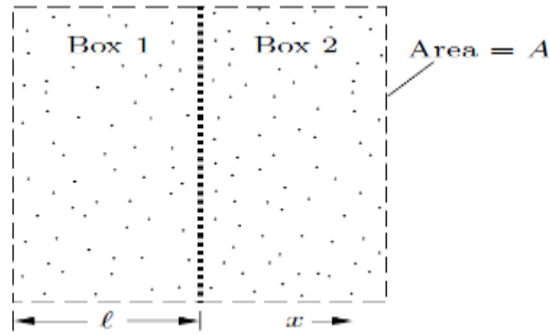
Figure 2.14 A partition of a room of gas. Copyright © 2000, Addison Wesley.

We can use these basic facts to determine the rate of heat transfer across a small room of gas. Here, let's suppose we partition the room of gas and suppose that box 1 has internal energy U_1 and box 2 has internal energy U_2 (where $U_1 > U_2$), as shown in Figure 2.14. Heat conduction occurs in this scenario because the molecules moving from box 1 to box 2 have a different average energy from the molecules moving from box to box 1. Since the motion is statistically random, we have

$$\Delta Q = \frac{1}{2}(U_1 - U_2) = -\frac{1}{2}C_V(T_2 - T_1) = -\frac{1}{2}C_V l \frac{dT}{dx}$$

where it is assumed that the molecules are traveling across a distance l. Thus, the rate of heat flow is given by

$$\frac{\Delta Q}{\Delta t} = -\frac{1}{2}\frac{C_V l}{\Delta t}\frac{dT}{dx} = -\left(\frac{1}{2}\frac{C_V l}{A \Delta t}\right)A\frac{dT}{dx} \equiv -k_t A\frac{dT}{dx}$$

Here k_t is defined as the **thermal conductivity** and it is a measure of thermal conductive properties of the material. This expression is known as **<u>Fourier's law of heat conduction</u>** and it illustrates three basic principles of heat conduction

- Heat flow is proportional to the temperature gradient
- Heat flow depends on the thermal conductivity of the substance
- Heat flow always flows from hot to cold objects

Using kinetic theory and the ideal gas law, we can write the thermal conductivity can be written as

$$k_t = \frac{1}{2}\frac{C_V l}{A \Delta t} = \frac{1}{2}\frac{C_V}{V}l\bar{v} = \frac{1}{4}\frac{fP}{T}l\bar{v} \propto f\sqrt{T}$$

49

Thus, thermal conductivity varies as $T^{1/2}$, which is confirmed for many gases, as shown in Figure 2.15.
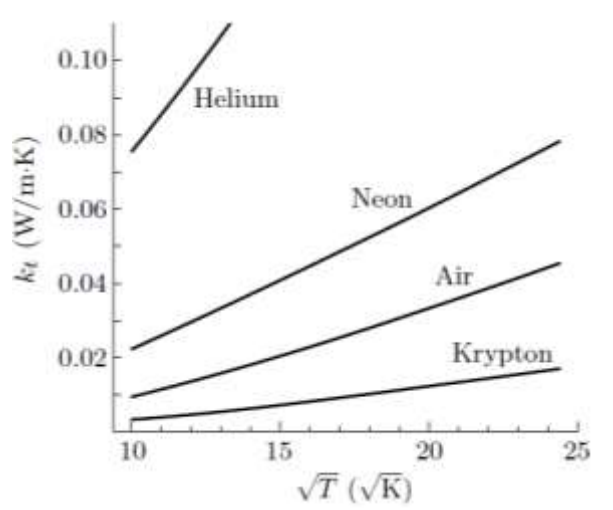
Figure 2.15 The thermal conductivity of selected gases vs. the square root of the absolute temperature

A simple example of heat conduction is of a solid rod of uniform cross-sectional area as shown in Figure 2.16, one end of which (the left) is maintained at a high temperature and the other end (right) at a lower temperature. In the steady state the temperature does not depend on time. This is possible only if the quantity of energy entering a given region is precisely equal to the energy leaving the region. Since the cross-sectional area is uniform throughout the rod, it follows that dT/dx must also be constant. Then we could replace

$$\frac{dT}{dx} = \frac{T_2 - T_1}{L}$$

where $T_{1,2}$ are the temperatures of the extremities as shown. Notice that $dT/dx < 0$ is negative if energy is flowing to the right. This justifies the negative sign: its presence indicates that energy flows in the direction of decreasing temperature. Thus,

$$Q = -\sigma(T_2 - T_1)$$

where $\sigma = k_t A/L$ is called the **conductance** of the material. Its reciprocal is called the **resistance**, R, of the material.
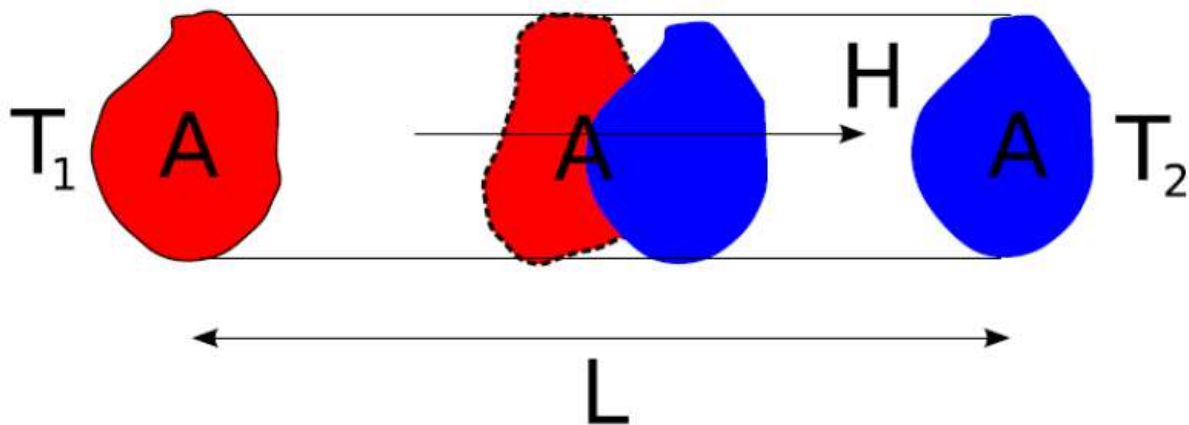
Figure 2.16 Heat conduction across a solid of uniform cross sectional area

2.4.2 Convection

Figure 2.17 Schematic of heat transfer mechanism associated with heating a pot of water

Energy transfer between two or more macroscopic systems, or within a single macroscopic system that is not in equilibrium, by the gross movement of the substance(s) composing the system(s), is called **convection**. A typical example of convection occurs when boiling water in a vessel from below, as shown in Figure 2.17. Energy is transferred to the lowest layer of the water in the vessel by conduction. As the layer warms up it expands and its density

decreases causing it to rise by Archimedes' principle. Cooler layers above it descend to take its place and get warmed by contact with the base of the vessel. In this way there is a gross movement of the water which eventually transfers the energy being supplied through the base to the entire volume of water in the vessel. Convection is employed by radiators, which warm a room by warming the air in contact with them. The hot air then rises allowing colder air to take its place close to the radiator, thus setting up a circulation. Wind currents, ocean currents etc., are all examples of convection.

Convection is responsible for energy transfer in the sun and in any main sequence star, occurring in a spherical shell, whose thickness is about 200,000 km, that lies between a region dominated by radiation and adjacent to the fusing core, called the radiation zone, and the photosphere, which is, roughly speaking, the thin, visible layer (about 100 km) of gas on the surface of the sun from which photons are able to escape freely. The range of radii in which the energy is transferred primarily by convection is called the **convection zone**. In this region, mass movement of the plasma within the star forms a circular current in which the heated plasma at the bottom rises and cooler plasma that has passed its energy into the photosphere descends. Convective heat transfer occurs whenever there is the possibility of a flow and when the temperature gradient is high enough.

Recall that the law of atmospheres from Chapter 1

$$\frac{dP}{dz} = -\frac{\langle m \rangle g}{kT} P \Rightarrow P(z) = P(0) \exp\left(-\frac{\langle m \rangle gz}{kT}\right)$$

This indicates that pressure decreases with height in the atmosphere. Ordinarily, the temperature of the bottommost 10-15 km of the atmosphere (called the **troposphere**) decreases with altitude due to heating from the ground. If an air parcel (i.e. an infinitesimal insulated volume of air) rises in the atmosphere, it will enter a region in which the environmental pressure is less than the pressure inside the parcel, causing the air parcel. Since the air parcel is doing work on the environment, the energy needed to produce a volume expansion must come at the expense of the parcel's own internal energy. Therefore, rising air parcels lose internal energy and thus, cool. If the air parcel remains warmer than the surrounding air, then the air parcel will continue to rise. In other words, if the environmental temperature gradient exceeds a certain critical value, then convection will occur such that warm, low-density air will rise, while cool, high-density air sinks. Using kinetic theory and the first law of thermodynamics, we can derive the condition for spontaneous convection of dry air in Earth's atmosphere.

For an ideal gas exchanging no heat with the environment, the 1st law gives
$$dU = -P \, dV$$

For an ideal gas, the internal energy can be written as

$$dU = \frac{f}{2} Nk \, dT$$

We can write the work term as

$$P \, dV = d(PV) - V \, dP = Nk \, dT - V \, dP = Nk \, dT - NkT \frac{dP}{P}$$

Combining these expressions give

$$\frac{f}{2} Nk \, dT = -Nk \, dT + \frac{NkT}{P} dP \Rightarrow dT = \frac{2}{f+2} \frac{T}{P} dP$$

Applying the barometric equation gives

$$dT = -\frac{2}{f+2} \frac{\langle m \rangle g}{k} dz \Rightarrow \frac{dT}{dz} = -\frac{2}{f+2} \frac{\langle m \rangle g}{k} = -\frac{2}{f+2} \frac{Mg}{R_d}$$

Here, $M = 29 \, g/mol$ is the molar mass of dry air. Since air is composed primarily of diatomic molecules (78% N_2 and 20% O_2), $f = 5$ and the critical temperature gradient is given by

$$\frac{dT}{dz} = -\frac{2}{5+2} \frac{\left(0.029 \frac{kg}{mol}\right)\left(9.8 \frac{m}{s^2}\right)}{\left(8.315 \frac{J}{mol \cdot K}\right)} = -9.8 \frac{K}{km}$$

Note that the temperature gradient is independent of temperature and pressure. This quantity is known as the **dry adiabatic lapse rate.** This expression states that if lapse rate in the atmosphere is greater than $9.8 \, K/km$, then a rising air parcel will continue to accelerate upward in the atmosphere and there will be free, spontaneous convection. We will give a description of spontaneous convection of moist air during our discussion on phase equilibria.

2.4.3 Radiation

A third means of energy transfer is by **thermal radiation**. In a hot body, energy is distributed randomly between its constituent atoms and molecules. This energy causes the charges within the body to oscillate and the oscillating charges then emit electromagnetic waves. When the ensuing radiation is in thermal equilibrium with its source, it is said to be "thermal".
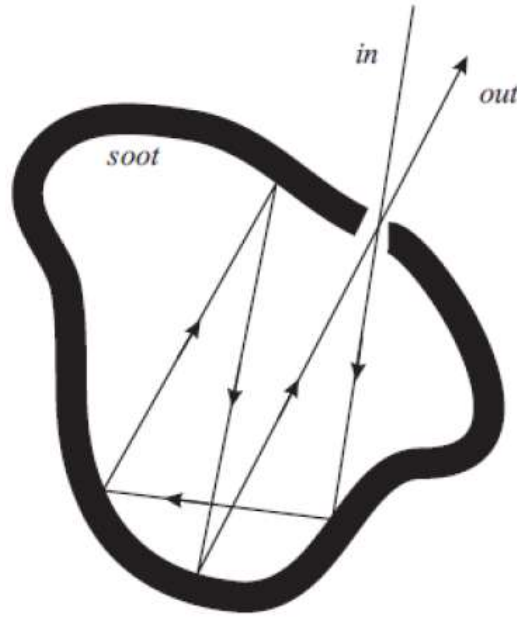
Figure 2.18 Schematic of a cavity

Every radiating body can be characterized by its absorptivity and its emissivity. The absorptivity, a, of a body is the fraction of incident radiant energy that it is able to absorb. An ideal black body is defined to be a perfect absorber, i.e., one that absorbs all of the incident radiant energy, so for such a body $a = 1$. Real objects have some reflectivity and are not perfect black bodies. The closest approximation to a perfect black body would be a cavity, i.e., a small hole leading to the inside of a hollow object that is coated with some amorphous black material, such as soot. Radiation incident on the hole from the outside is reflected a large number of times on the interior walls as shown in Figure 2.18. During each collision the walls will absorb some of the incident radiation and hence the cavity acts as a perfect absorber. If the temperature of the cavity is above that of its environment, radiation may leave the cavity only after multiple reflections with the walls during which it achieves thermal equilibrium with them. It is therefore characterized exclusively by the temperature of the cavity walls and does not depend on the material of which they are made. The spaces within the pores of hot charcoal behave like small cavities, emitting radiation that is characterized only by the temperature of the coal.

The rate at which an object an object radiates energy is proportional to the fourth power of its absolute temperature. This is known as **Stefan's law** and is expressed in equation form as

$$\mathbb{P} = \sigma A e T^4$$

where $\mathbb{P}$ is the power in Watts radiated by the object, σ is a constant, A is the surface area of the object in square meters, e is the emissivity constant, and T is the surface temperature in kelvins. The value of the emissivity can vary between zero and unity, depending on the properties of the surface of the object. The emissivity is equal to the fraction of the incoming radiation that the

surface absorbs. We will give a complete description of blackbody radiation during our discussion on classical statistical mechanics.

Based on our understanding of the first law of thermodynamics, we can examine the work done by a given system, the heat exchanged between the system and its environment, and the change of internal energy of the system undergoing any quasistatic thermodynamic process. In general, knowing the thermodynamic process is the equivalent to having an additional constraint on the thermodynamic system, which can be used to derive additional equations of state. In the next chapter, we will examine the basic quasistatic thermodynamic processes and apply them to the operation of thermodynamic cycles (such as heat engines). This will lead us to an expression for the second law of thermodynamics.

Chapter 3: Thermodynamic Cycles and the 2nd Law

The only restriction that the first law of thermodynamics places on a process is that energy should be conserved. One consequence, for example, is that it prohibits any cyclic process from performing mechanical work without extracting energy (e.g. in the form of heat) from some source. A cycle that is capable of performing mechanical work without extracting energy from any source, were it possible, would be called a **perpetual motion machine of the first kind.** The first law assures us that such a cycle does not exist.

However, we could imagine the exciting possibility of a machine that extracts energy from a reservoir of some sort and transforms all of the extracted energy into useful mechanical work with no other effect. We could also (for all practical purposes endlessly) extract energy from some reservoir of energy, convert all the extracted energy into useful work and then transfer that energy back into the reservoir from which we extracted it in the first place. This kind of a cycle is called a **perpetual motion machine of the second kind**. Experience teaches us that a perpetual motion machine of the second kind also does not exist: every heat engine we have built involves a transfer of energy from some "hotter" reservoir of energy (e.g. gasoline in an automobile) to a ``colder" one (e.g. the atmosphere, for most engines). A perpetual motion machine of the second kind would need just one reservoir of energy.

These examples demonstrate that the first law is only a *necessary* condition for the occurrence of a thermodynamic process, not a sufficient one. The impossibility of the processes described in the examples above is captured by the **second law of thermodynamics**. In this chapter, we will introduce the second law of thermodynamics by the limitations of all thermodynamic cycles. In doing so, we will discuss two equivalent statements of the second law of thermodynamics, which involve the operation of heat engines and refrigerators. We start by discussing basic thermodynamic processes.

3.1 Thermodynamic Processes

Recall that a thermodynamic process is any process that takes a macroscopic system from one equilibrium state to another. Therefore, a thermodynamic process is any process that produces a continuous curve in thermodynamic phase space, as shown in Figure 3.1. As mentioned in the last chapter, knowing the thermodynamic process is the equivalent to having an additional constraint on the thermodynamic system, which can be used to derive additional

equations of state. In this section we will restrict our attention to an ideal gas and examine four basic quasi-static thermodynamic processes: isochoric processes, isothermal processes, isobaric processes, and adiabatic processes.

For quasi-equilibrium processes, **P**, **V**, **T** are **well-defined** – the "path" between two states is a *continuous lines* in the **P**, **V**, **T** space.
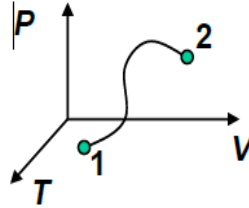
Figure 3.1 Schematic of a thermodynamic process in thermodynamic phase space

3.1.1 Isochoric Processes
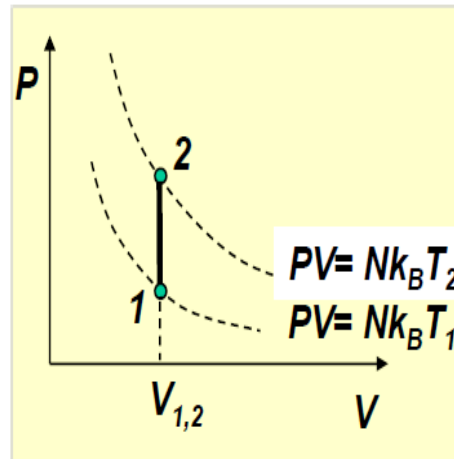
Figure 3.2 Isochoric process on a PV diagram

An **isochoric process** is a thermodynamic process during which the volume of the closed system remains constant, as in Figure 3.2. Thus, for an isochoric process, no work is done since $dV = 0$. Therefore, according to the first law,

$$dU = \delta Q \Rightarrow \Delta U = C_V \Delta T$$

This result states that any change in the internal energy (and thus change in the temperature) is directly related to heat exchange between the system and its environment. Thus, heat added to

(removed from) the system leads to an increase (decrease) in temperature of the system. Since volume is constant for an isochoric process, it can be shown that the isochoric equation of state takes the form $P/T = const.$, which is the equivalent of Charles' law.

3.1.2 Isothermal Processes
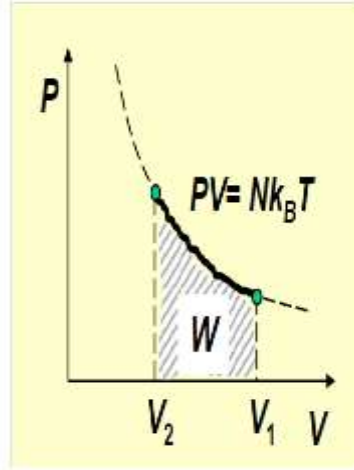
Figure 3.3 Isothermal process on a PV diagram

An **isothermal process** is a thermodynamic process during which the temperature of the closed system remains constant, as in Figure 3.3. For an isothermal process, the internal energy of an ideal gas remains constant since $U = U(T)$, implying that $dU = 0$. Therefore, according to the first law

$$\delta Q = -\delta W \Rightarrow Q = \int_{V_i}^{V_f} P \, dV = NkT \ln \left(\frac{V_f}{V_i} \right)$$

This result states that any heat exchanged between the system and its environment results in work done by the gas. Thus, heat added to (removed from) the gas causes an expansion (or compression) by the gas. In order for an ideal gas to maintain a constant temperature while absorbing heat, it must do work on the environment (which is normally a cooling process). Conversely, in order for an ideal gas to maintain a constant temperature while releasing heat, work must be done by the environment on the gas (which is normally a warming process). For this reason, isothermal expansions/compressions tend to be slowly evolving processes. Since

temperature is constant for an isothermal process, it can be shown that the isothermal equation of state takes the form $PV = const.$, which is the equivalent of Boyle's law.

3.1.3 Isobaric Processes
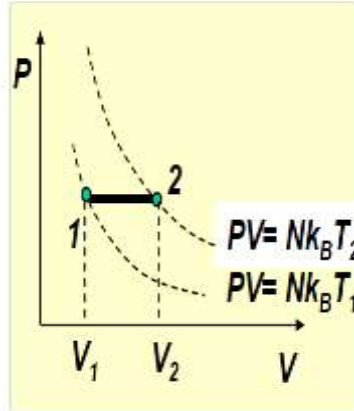
Figure 3.4 Isobaric process on a PV diagram

An **isobaric process** is a thermodynamic process during which the pressure of the closed system remains constant, as in Figure 3.4. For an isobaric process, the first law can be written as

$$dU = \delta Q + \delta W \Rightarrow \Delta U = C_P \Delta T - P \Delta V$$

This result states that any expansion (compression) of an ideal gas will lead to an decrease (increase) in the internal energy of an ideal gas. The above expression can be written strictly as a function of temperature

$$\Delta U = C_P \Delta T - P \Delta V = (C_P - Nk)\Delta T = C_V \Delta T$$

which gives the expression that we obtained earlier. Thus, increasing (decreasing) the temperature of an ideal gas leads to an increase (decrease) in the internal energy of the gas. Since pressure is constant for an isobaric process, it can be shown that the isobaric equation of state takes the form of $V/T = const.$, which is the equivalent of the Guy-Lussac's law.

3.1.4 Adiabatic Processes

A thermodynamic process in which no energy is transferred to a system except by work is said to be **adiabatic** and the system is then said to be *thermally isolated*. Therefore, for an adiabatic process, $\delta Q = 0$. For an adiabatic process, the first law can be written as

$$dU = \delta W \Rightarrow \frac{f}{2} Nk \, dT = -P \, dV$$

This expression states that any change in the internal energy of an ideal gas (and thus the temperature) is due to the work done by the gas on the environment. Thus, an adiabatic expansion (compression) of an ideal gas leads a decrease (increase) in internal energy.

We can derive an equation of state associated with an ideal gas undergoing an adiabatic process. For any adiabatic process with a given equation of state, we can write the

$$\delta Q = dU - dW = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + P \, dV = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV = 0$$

Using the chain rule, we have

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + P\right] dV = 0$$

For an ideal gas, we note that

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{Nk}, \quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{Nk}$$

Therefore, we have

$$\frac{C_V}{Nk} V \, dP + \left[\frac{C_V}{Nk} + 1\right] P \, dV = 0 \Rightarrow \frac{C_V}{Nk} V \, dP + \frac{C_P}{Nk} P \, dV = 0$$

Rearranging gives

$$\frac{dP}{P} = -\frac{C_P}{C_V} \frac{dV}{V} \Rightarrow PV^\gamma = constant \quad (3.1)$$

where $\gamma = C_P/C_V$. Equation (3.1) is known as **the adiabatic equation of state**, applicable only to ideal gases undergoing adiabatic processes. The adiabatic equation of state adds an additional constraint on the system, which can be used to eliminate one of the three state variables and re-

express the equation of state in terms of the other two. Thus, the adiabatic equation of state can be written in terms of (P, T) and (T, V):

$$P^{\gamma-1}T^{\gamma} = constant, \quad TV^{\gamma-1} = constant$$

These expressions, known as **Poisson relations**, are relations between all pairs of three thermodynamic state variables P, V, and T for an ideal gas undergoing an adiabatic process.

The adiabatic equation of state leads to the expression for work

$$W = -\int P \, dV = -K \int_{V_i}^{V_f} V^{-\gamma} \, dV = -K\frac{V_f^{1-\gamma} - V_i^{1-\gamma}}{1-\gamma}$$

where K is the constant from Equation (3.1). This expression states that the amount of work needed to change the state of a thermally isolated system depends only on the *initial* and *final* states and not on the *intermediate* states. With our expression for work, we can write the first law for an ideal gas undergoing an adiabatic process as

$$\Delta U = W \Rightarrow \frac{f}{2}Nk \, \Delta T = -K\frac{V_f^{1-\gamma} - V_i^{1-\gamma}}{1-\gamma}$$

Thus, as stated earlier, an adiabatic expansion (compression) of an ideal gas leads a decrease (increase) in internal energy (and temperature) of an ideal gas.

Contrary to slowly-evolving isothermal processes, adiabatic expansion/compression tend to be rapidly-evolving processes. During a rapid expansion/compression of a gas, there is usually not enough time for heat exchange to occur between a system and its environment and thus, these processes are functionally adiabatic. In response to the rapid expansion/compression of a gas, there is a corresponding change in internal energy. This can also be seen by observing the $P - V$ diagram for an adiabatic process versus an isothermal process, as shown in Figure 3.5.
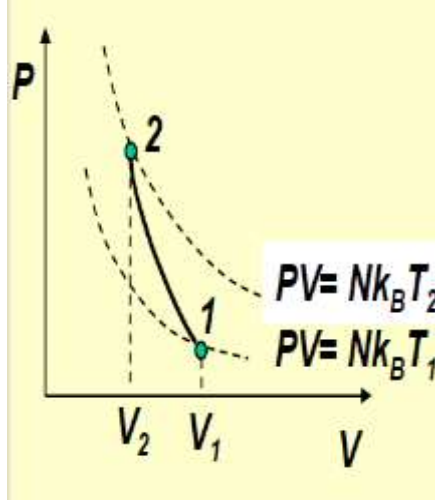
Figure 3.5 Adiabatic compression on a PV diagram

Notice that the PV curve for the adiabatic process has a higher slope than an isotherm. In other words, the adiabat begins on a lower-temperature isotherm and ends on a higher temperature isotherm. For an adiabatic process, the work flowing into the gas by the compression causes an increase in temperature. Conversely, for an adiabatic expansion, the work flowing out of the gas comes at the expense of its thermal energy, cause a decrease in temperature.

The Poisson relation between pressure and temperature motivates the introduction of a new variable, one that is conserved during an adiabatic process. The **potential temperature** θ is defined as that temperature the system would assume were it compressed or expanded adiabatically to a reference pressure (usually $P_0 = 1000\ hPa$). An adiabatic process from the state (P, T) to the reference state (P_0, θ) satisfies the Poisson relation

$$\theta P_0^\kappa = T P^\kappa$$

where $\kappa = (\gamma - 1)/\gamma$. Hence, the potential temperature is described by

$$\theta = T \left(\frac{P_0}{P} \right)^{-\kappa}$$

A function of pressure and temperature, θ is a state function. According to the above expression, θ is invariant along an adiabatic path in thermodynamic phase space. The concept of potential temperature applies to any stratified fluid and is most frequently used in the atmospheric sciences and oceanography. Potential temperature can be used as a tracer during adiabatic processes and can be used to identify diabatic processes (i.e. processes that involves exchanges with heat).

During diabatic conditions (i.e. conditions where heat is exchanged with the environment), θ is no longer conserved. Instead, θ changes in proportion to the heat transferred into the parcel. To show this, we note that the expression for θ can be written as

$$d \ln \theta - d \ln T = -\kappa \, d \ln P$$

Using the first law of thermodynamics and the ideal gas law leads to a similar relation

$$d \ln T - \kappa \, d \ln P = \frac{\delta Q}{C_P T}$$

Combining both expression then yields

$$d \ln \theta = \frac{\delta Q}{C_P T}$$

Therefore, potential temperature increases in direct proportion to the heat transferred into an isolated system (e.g. in proportion to its departure from adiabatic conditions).

3.2 Thermodynamic Cycles
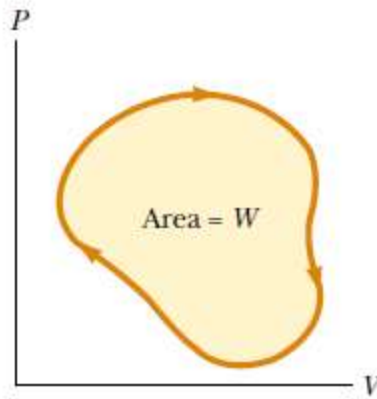
Figure 3.6 A thermodynamic cycle on a PV diagram

A **thermodynamic cycle** is a process in which the thermodynamic system (we will sometimes refer to the thermodynamic system as the working substance) periodically returns to its original macrostate. As we will shortly show, any system undergoing a cyclic process will either do work on the environment or have work done upon it by the environment. By the first law of thermodynamics, if work is done by the cycle then the energy for the work done must be extracted from some external source. To simplify matters we will work with **heat reservoirs**. A heat reservoir is a thermodynamic system with a very large heat capacity compared with the working substance, so that any exchange of heat between the substance and the reservoir will

result in no significant change in the reservoir's temperature. Thus heat reservoirs maintain their temperature no matter how much energy is extracted or deposited into them.

We begun our study of classical thermodynamics by saying that one of its principle objectives is to better understand processes that transform heat into useful work and vice-versa. Let us therefore get a better look at these processes. A cyclic process would be represented by a closed curve in the thermodynamic phase space. This follows from the requirement that the thermodynamic system should periodically return to its initial state. Upon completion of a cycle, the state properties do not change and the engine is able to repeat the cycle. However, path dependent quantities, such as heat and work do change during each cycle, and so may change indefinitely as the cycle repeats itself. The closed curve representing a cycle separates the PV plane into two regions, an "interior" and an "exterior". The work done,

$$W = -\oint_C P \, dV$$

where C represents the closed curve in the PV plane will always be the area of the interior region. This assumes that the only way a system may do external work is through changes in the volume. In general there may be several external parameters, X_i, whose change requires the system to do work on the environment. In that case, the work done is given by

$$W = -\oint_C \sum_i P_{X_i} \, dX_i$$

where P_{X_i} represents the generalized force corresponding to changes in X_i. In what follows, the expression $P \, dV$ will be understood to represent $\sum_i P_{X_i} \, dX_i$ whenever we work with systems in which the volume is not the only external variable whose change involves external work.
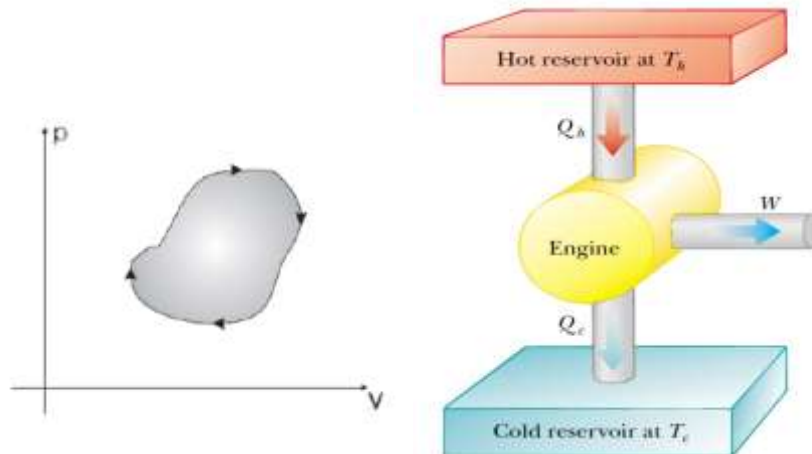
Figure 3.7 A cycle and schematic representing a heat engine: $T_h > T_l$
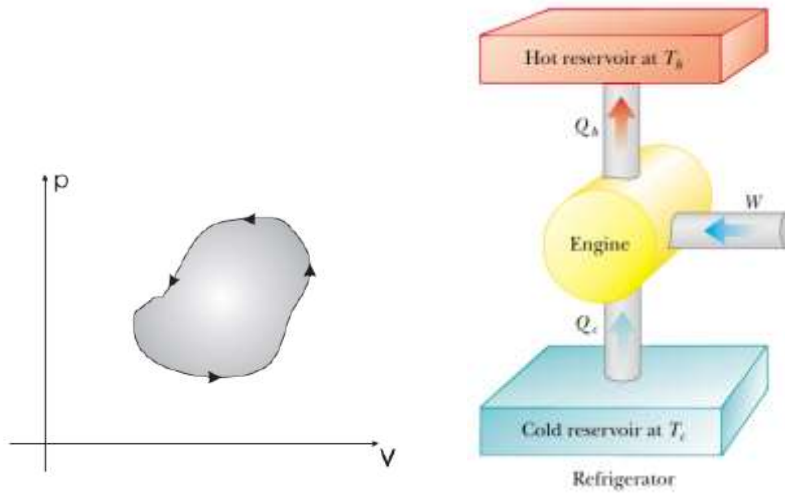
Figure 3.8 A cycle and schematic representing a refrigerator: $T_h > T_l$

If the cycle operates in a clockwise direction, then the work done is negative, which implies that the cycle does work against the environment. In this case, the cycle is a heat engine (see Figure 3.7). Thus, we define a **heat engine** as any thermodynamic cycle which extracts energy from a reservoir in the form of heat and performs mechanical work. On the contrary, if it operates in a counterclockwise direction, the work done is positive, which implies that environment does work on the system. In this case, the cycle will be a refrigerator (see Figure 3.8). Thus, we define a **refrigerator** will be any thermodynamic cycle which transfers energy in the form of heat from a reservoir at a lower temperature to a reservoir at a higher temperature.

Let's examine the heat engine in more detail. We will define Q_h for the heat absorbed from the hot reservoir in some given time period, Q_c for the heat expelled to the cold reservoir, and W as the net work done by the engine during this time. ***For the entirety of this chapter, we take Q_c, Q_h, and W to be positive quantities*** (note this is a departure from the earlier sign conventions developed in Chapter 2). Since the internal energy is a function only of the state variables, this implies that $\Delta U = 0$ at the completion of each cycle. Thus according to the first law of thermodynamics and using the sign conventions of this chapter, $W = Q_h - Q_c$ at the completion of each cycle. The **efficiency** of any thermodynamic cycle is supposed to provide some measure of how well the cycle accomplishes its purpose. For a heat engine, the purpose is to do useful work, and thus its efficiency would be

$$e_h = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

which is always between zero and 1, since $Q_c \geq 0$ and $0 \leq Q_c \leq Q_h$. An efficiency of unity would represent an ideal heat engine that is able to convert *all* of the supplied energy into useful work. An efficiency of zero is the other limit in which no work is done for the energy supplied.

The purpose of a refrigerator, on the other hand, is to remove energy in the form of heat from some reservoir at a lower temperature and deposit it into a reservoir at a higher temperature. The efficiency of the cycle should be defined as

$$e_r = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \left(\frac{Q_h - Q_c}{Q_c}\right)^{-1} = \left(\frac{Q_h}{Q_c} - 1\right)^{-1}$$

Because $W \geq 0$ for the refrigerator (since work must be done from an outside source on the refrigerator in order for it to operate), we must have $Q_c < Q_h$ and it follows that the efficiency of a refrigerator can be any non-negative real number. A perfect refrigerator would require no work to be done and so have an infinite efficiency. An efficiency of zero would represent the opposite limit in which an infinite amount of work must be done on the refrigerator to accomplish the transfer of any energy.

It is also helpful to think of the efficiency of a refrigerator in terms of a benefit to cost ratio. For the refrigerator, the benefit is the Q_c while the cost is W. This ratio is called the **coefficient of performance** and it is identical to the efficiency of a refrigerator given above. As we will see in the next chapter, the efficiencies derived above are the lower-limit for all real heat engines and refrigerators due to the second law of thermodynamics. Let's now consider some concrete examples of heat engines and refrigerators. We begin with the standard engine, the Carnot cycle, whose great advantage as we will see later is that it operates between just two heat reservoirs and, thus, between two temperatures.

3.3 The Kelvin-Planck and Clausius Statements

The above section shows that a perfect refrigerator or heat engine can be constructed if no heat flows out of the system. However, experience has taught us that for any real engine, there is always heat exhaust, regardless of the working substance of the engine. These limitations lead to the two original statements of the **second law of thermodynamics**. The first is due to the British physicist and engineer William Thomson (also named Lord Kelvin) and concerns heat engines:

The Kelvin-Planck Statement: A transformation whose *only* effect is to transform energy extracted from a body in the form of heat into useful work is impossible
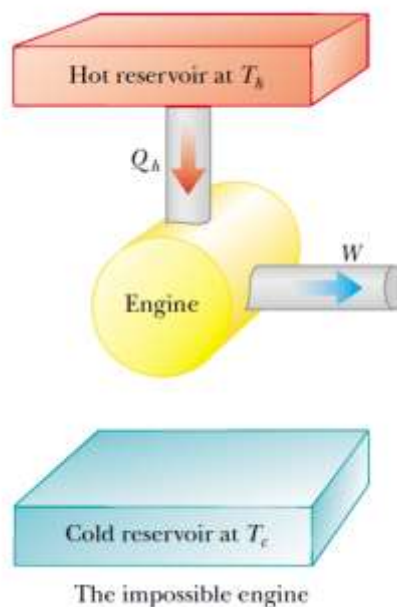
Figure 3.9 Schematic of the Kelvin-Planck statement

The Kelvin-Planck statement of the second law states that there are limits to the efficiency of heat engines, i.e., the efficiency of any heat engine must always be less than 100%. Some energy must always be lost to the environment. Therefore, it's theoretically impossible to construct a heat engine with 100% efficiency.

The second statement of the second law is due to the German physicist Rudolf Clausius and concerns refrigerators.

The Clausius Statement: A transformation whose *only* effect is to transfer energy in the form of heat from a body at a given temperature to a body at a higher temperature is impossible.
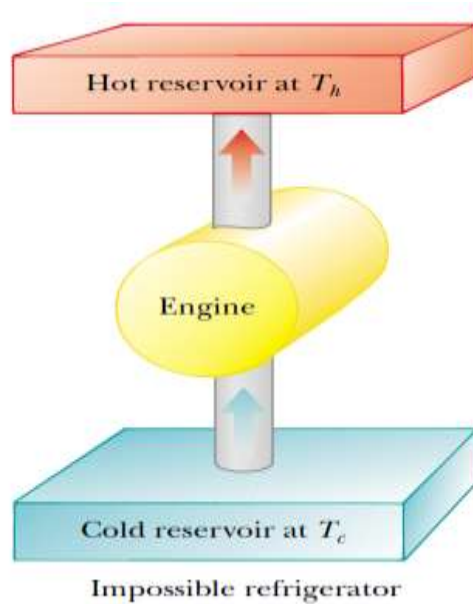
Figure 3.10 Schematic of the Clausius statement

The Clausius statement of the second law states that heat *spontaneously* flows from hotter objects to cooler objects. Here, spontaneous means that the energy transfer occurs naturally without work being done. Therefore, in order for heat to flow from cooler objects to warmer objects, work must be done to transfer thermal energy. This implies that it is impossible to construct any device (such as a refrigerator or heat pump) that spontaneously causes the net thermal energy to flow from a cooler object to warmer object with performing work on the system.

Although these two statements appear different, they are indeed quite rigorously equivalent to each other. We will prove this in two parts: First, we'll show that if the Kelvin-Planck statement is *not* true, then the Clausius statement cannot be true. Then we will show that if the Clausius statement is *not* true, then the Kelvin-Planck statement cannot be true either.
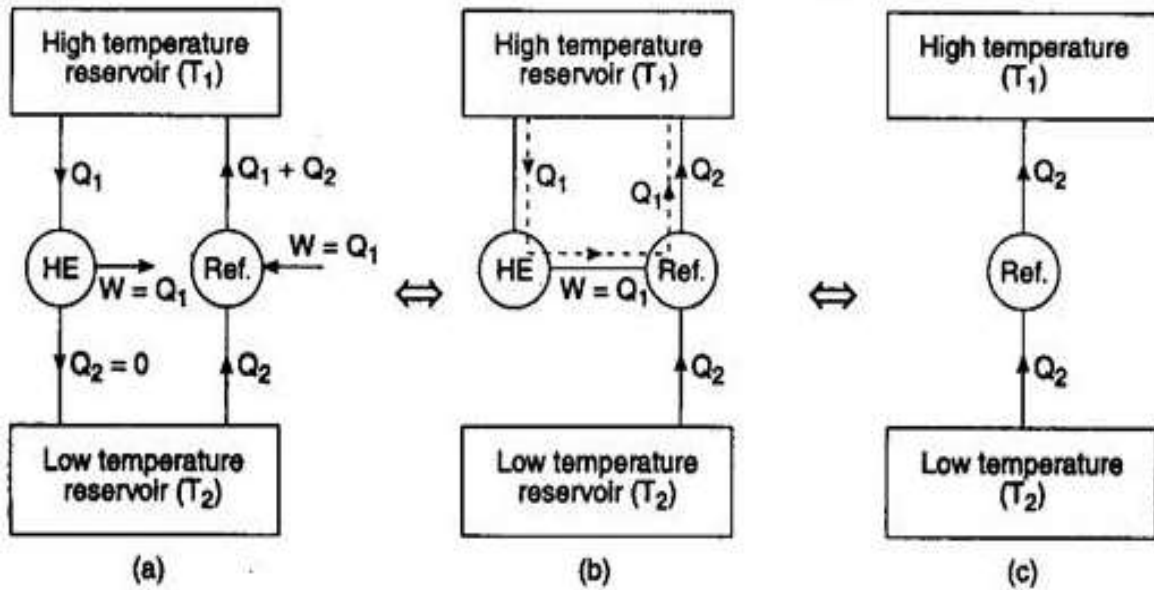
Figure 3.11 Proof that violation of Kelvin-Planck statement leads to the violation of the Clausius statement

Let's assume that the Kelvin-Planck statement of the second law is *not* true, as shown in Figure 3.11. This means that it's possible, in principle, to transform energy absorbed as heat from a reservoir at some temperature (T_1) into useful work with *no other effect*, i.e., the transformation occurs with 100% efficiency, as shown in Figure 3.11(a). Of course, the mechanical work produced can now be transferred to a body at another temperature (say T_2) by friction (as in the Joule paddlewheel experiment). This transfer of energy takes place *no matter what the temperature T_2*. Let's suppose we use the mechanical work from the original heat engine to operate a refrigerator, as shown in Figure 3.11(a). As the refrigerator extract Q_2 from the cold reservoir and uses Q_1 to operator, the energy that is transferred to the hot reservoir must be $Q_1 + Q_2$ by the first law of thermodynamics. The combined effect of heat engine and the refrigerator is shown in Figure 3.11(b), in which we see that the net heat returning to the hot reservoir is $Q_{net} = Q_2$. Thus, the overall effect of the entire process is to transfer heat Q_2 from the low temperature reservoir to the high temperature reservoir with no other net effect, as shown in Figure 3.11(c). This contradicts the Clausius statement.

Let's assume that the Clausius statement of the second law is *not* true, as shown in Figure 3.12. This means that it is possible to transfer heat from a body at a lower temperature (T_2) to a body at a higher temperature (T_1), i.e. the transformation occurs spontaneously. Let's suppose we connect a heat engine operating between those two temperatures to the heat pump, as shown in Figure 3.12(a). Thus, the heat engine extracts $Q_1 + Q_2$ from the hot temperature reservoir and it can convert part of this into useful work. The combined effect of heat engine and the heat pump is shown in Figure 3.12(b), in which we see that the net heat extracted from the hot temperature reservoir is Q_1 (since the body at T_1 absorbs a certain quantity of energy and then

releases the same quantity of energy, no change has occurred in its state). The result is that we have a process whose net effect is to transform heat absorbed from the high temperature reservoir completely into useful work, as shown in Figure 3.12(c). This contradicts the Kelvin-Planck statement and completes our proof.
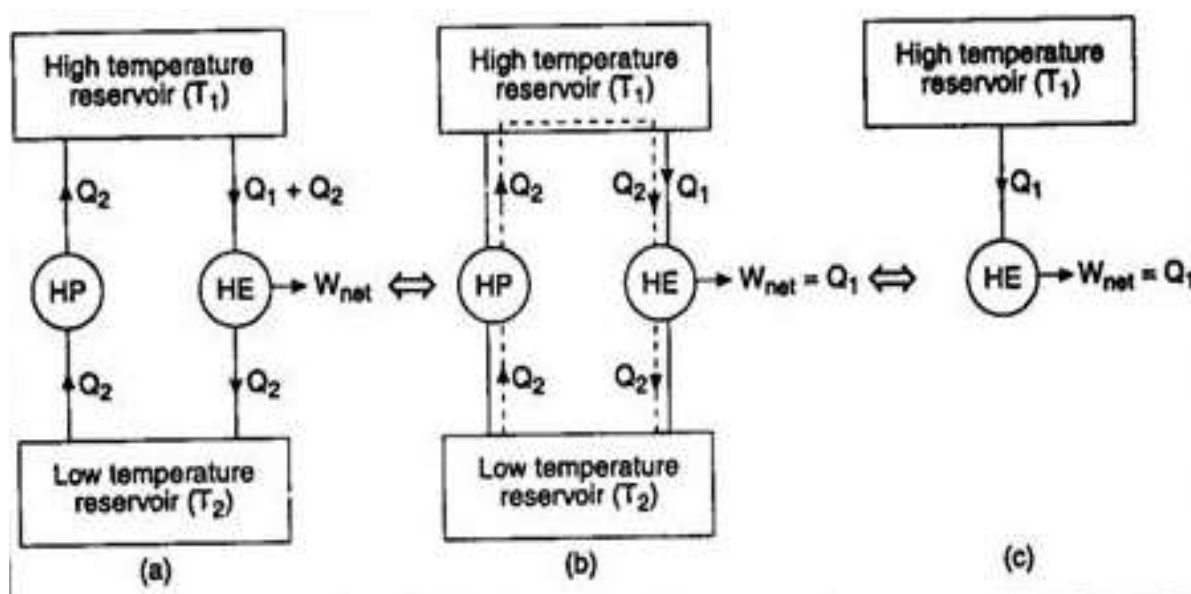
Figure 3.12 Proof that violation of Clausius statement leads to the violation of the Kelvin-Planck statement

These equivalent statements of the second law lead to the following question: what is the most efficient thermodynamic cycle and what is the maximum thermodynamic efficiency for a given cycle? These questions were answered by Carnot and the development of the Carnot cycle.

3.4 The Carnot Cycle

In 1824 a French engineer named Sadi Carnot described a theoretical engine, now called a Carnot engine, that is of great importance from both practical and theoretical viewpoints. He showed that a heat engine operating in an ideal, reversible cycle called a **Carnot cycle** between two energy reservoirs is the most efficient engine possible. Such an ideal engine establishes an upper limit on the efficiencies of all other engines. That is, the net work done by a working substance taken through the Carnot cycle is the greatest amount of work possible for a given amount of energy supplied to the substance at the upper temperature. Carnot's theorem can be stated as follows:

No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs

Before we discuss Carnot's theorem and discuss the features of the Carnot cycle, we need to provide a background on reversible and irreversible processes.

3.4.1 Reversible and Irreversible Processes

In a **reversible process**, the system undergoing the process can be returned to its initial conditions along the same path shown on a *PV* diagram, and every point along this path is an equilibrium state. In other words, a reversible process is a process in which both the system and the environment can be returned to the original state by means of quasi-static processes. A process that does not satisfy these requirements is **irreversible**.

All natural processes are known to be irreversible. From the endless number of examples that could be selected, let us examine the adiabatic free expansion of a gas, which was already previously during the Joule free expansion experiment. The system that we consider is a gas in a thermally insulated container. A membrane separates the gas from a vacuum. When the membrane is punctured, the gas expands freely into the vacuum. As a result of the puncture, the system has changed because it occupies a greater volume after the expansion. Because the gas does not exert a force through a distance on the surroundings, it does no work on the surroundings as it expands. In addition, no energy is transferred to or from the gas by heat because the container is insulated from its surroundings. Thus, in this adiabatic process, the system has changed but the surroundings have not.

For this process to be reversible, we need to be able to return the gas to its original volume and temperature without changing the surroundings. Imagine that we try to reverse the process by compressing the gas to its original volume. To do so, we fit the container with a piston and use an engine to force the piston inward. During this process, the surroundings change because work is being done by an outside agent on the system. In addition, the system changes because the compression increases the temperature of the gas. We can lower the temperature of the gas by allowing it to come into contact with an external energy reservoir. Although this step returns the gas to its original conditions, the surroundings are again affected because energy is being added to the surroundings from the gas. If this energy could somehow be used to drive the engine that we have used to compress the gas, then the net energy transfer to the surroundings would be zero. In this way, the system and its surroundings could be returned to their initial conditions, and we could identify the process as reversible. However, the Kelvin–Planck statement of the second law specifies that the energy removed from the gas to return the temperature to its original value cannot be completely converted to mechanical energy in the

form of the work done by the engine in compressing the gas. Thus, we must conclude that the process is irreversible.

We could also argue that the adiabatic free expansion is irreversible by relying on the portion of the definition of a reversible process that refers to equilibrium states. For example, during the expansion, significant variations in pressure occur throughout the gas. Thus, there is no well-defined value of the pressure for the entire system at any time between the initial and final states. In fact, the process cannot even be represented as a path on a *PV* diagram. The *PV* diagram for an adiabatic free expansion would show the initial and final conditions as points, but these points would not be connected by a path. Thus, because the intermediate conditions between the initial and final states are not equilibrium states, the process is irreversible.
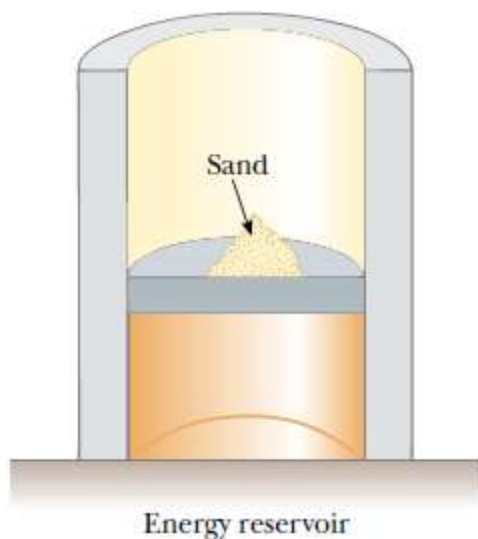
Figure 3.13 A gas in thermal contact with an energy reservoir is compressed slowly as individual grains of sand drop onto the piston. The compression is isothermal and reversible

Although all real processes are always irreversible, some are almost reversible. If a real process occurs very slowly such that the system is always very nearly in an equilibrium state, then the process can be approximated as reversible. For example, let us imagine that we compress a gas very slowly by dropping some grains of sand onto a frictionless piston, as shown in Figure 3.13. We make the process isothermal by placing the gas in thermal contact with an energy reservoir, and we transfer just enough energy from the gas to the reservoir during the process to keep the temperature constant. The pressure, volume, and temperature of the gas are all well defined during the isothermal compression, so each state during the process is an equilibrium state. Each time we add a grain of sand to the piston, the volume of the gas decreases

72

slightly while the pressure increases slightly. Each grain we add represents a change to a new equilibrium state. We can reverse the process by slowly removing grains from the piston.

A general characteristic of a reversible process is that no dissipative effects (such as turbulence or friction) that convert mechanical energy to internal energy can be present. Such effects can be impossible to eliminate completely. Hence, it is not surprising that real processes in nature are irreversible.

As a final point, it is important to distinguish between reversible and quasistatic processes. Reversible processes are always quasistatic, but not all quasi-static processes are reversible. For example, an infinitesimal compression of a gas in a cylinder where there exists friction between the piston and the cylinder is a quasistatic process, but not reversible process. Although the system has been driven from its equilibrium state by only an infinitesimal amount, heat has been irreversibly lost due to friction, and cannot be recovered by simply moving the piston infinitesimally in the opposite direction.

3.4.2 The Carnot Theorem
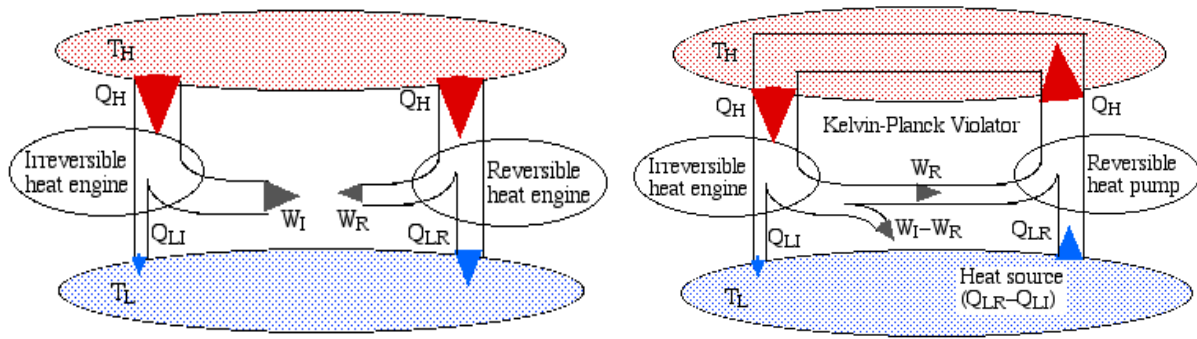
Figure 3.14 (Left) An irreversible engine and a reversible engine operating between the same two reservoirs. (Right) An irreversible heat engine and reversible heat pump operating between the same two reservoirs.

The simplest way to prove the Carnot theorem is to consider the scenario shown in Figure 3.14, in which we have an irreversible engine as well as a reversible engine operating between the same two reservoirs T_H and T_L. Let's suppose that the irreversible heat engine has a higher efficiency than the reversible engine. They both draw the same amount of heat Q_H from the high temperature reservoir, however the irreversible engine produces more work W_I than that of the reversible engine W_R. Note that the reversible engine by its nature can operate in reverse. Thus, if we use some of the work output W_R from the irreversible engine in order to drive the reversible engine, then it will operate as a heat pump, transferring heat Q_H to the high temperature reservoir. This causes the high temperature reservoir to become redundant, and the

net effect is that we extract a net amount of heat $\Delta Q = Q_{LR} - Q_{LI}$ from the low temperature reservoir in order to produce a net amount of work $W_I - W_R$. This is a violation of the Kelvin-Planck statement, thus proving Carnot's Theorem.

Suppose we replaced the irreversible engine in the above proof with another reversible engine. If the efficiencies of the two engines are not the same, then we can drive the reversible engine with the lower efficiency as a heat pump and produce a violation of the Kelvin-Planck statement just as above. This means that **all reversible heat engines operating between the same two heat reservoirs must have the same efficiency.**

3.4.3 The Efficiency of the Carnot Cycle
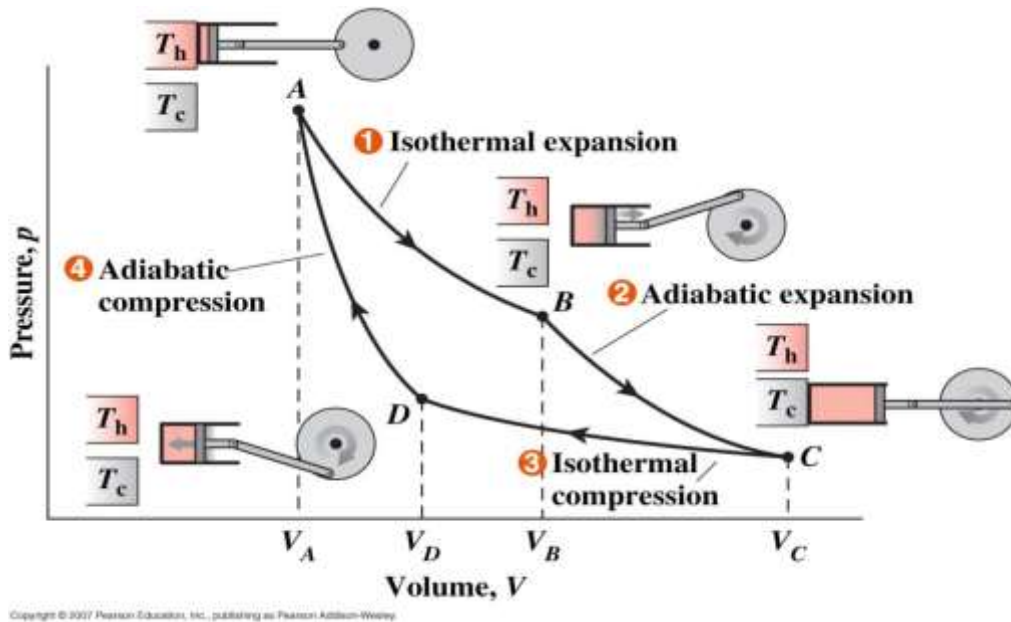
Figure 3.15 Schematic of the Carnot Cycle

Since the Carnot theorem guarantees that all reversible cycles operating between the same two reservoirs have the same efficiency, then our next step is to determine the efficiency of the Carnot cycle. The schematic of the Carnot cycle in Figure 3.15 shows that the Carnot cycle is a four-stage cycle composed of two isothermal processes and two adiabatic processes. Process $A \rightarrow B$ is an isothermal expansion at temperature T_h. The gas is placed in thermal contact with an energy reservoir at temperature T_h. During the expansion, the gas absorbs energy Q_h from the reservoir through the base of the cylinder and does work W_{AB} in raising the piston. During this phase,

$$Q_h = W_{AB} = NkT_h \int_{V_A}^{V_B} dV = NkT_h \ln\left(\frac{V_B}{V_A}\right)$$

In process $B \to C$, the base of the cylinder is replaced by a thermally nonconducting wall, and the gas expands adiabatically – that is, no energy enters or leaves the system. During the expansion, the temperature of the gas decreases from T_h to T_c and the work does W_{BC} in raising the piston. The change in internal energy during this phase

$$\Delta U_{BC} = W_{BC} = -\frac{K}{1-\gamma}\left(V_C^{\,1-\gamma} - V_B^{\,1-\gamma}\right)$$

Recall that the adiabatic equation of state

$$PV^\gamma = K \Rightarrow P = KV^{-\gamma}$$

Substituting into the above expression gives

$$\Delta U_{BC} = W_{BC} = -\frac{1}{1-\gamma}\left(V_C P_C - V_B P_B\right)$$

Using the ideal gas law gives

$$\Delta U_{BC} = W_{BC} = -\frac{Nk}{\gamma-1}\left(T_h - T_c\right)$$

In process $C \to D$, the gas is placed in thermal contact with an energy reservoir at temperature T_c and is compressed isothermally at temperature T_c. During this time, the gas expels energy Q_l to the reservoir, and the work done by the piston on the gas is W_{CD}. During this phase,

$$Q_l = |W_{CD}| = \left|NkT_c \int_{V_C}^{V_D} dV\right| = NkT_c \ln\left(\frac{V_C}{V_D}\right)$$

(Remember we take the absolute value of the work because we are defining all values of Q for a heat engine as positive in this chapter). In the final process $D \to A$, the base of the cylinder is replaced by a nonconducting wall, and the gas is compressed adiabatically. As a result the temperature of the gas increases to T_h, and the work done by the piston on the gas is W_{DA}. The change in internal energy during this phase

$$\Delta U_{DA} = W_{DA} = -\frac{K}{1-\gamma}\left(V_A^{\,1-\gamma} - V_D^{\,1-\gamma}\right) = \frac{Nk}{\gamma-1}\left(T_h - T_c\right)$$

Therefore, the Carnot efficiency is given by

$$e_c = 1 - \frac{Q_l}{Q_h} = 1 - \frac{NkT_c \ln\left(\frac{V_C}{V_D}\right)}{NkT_h \ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_c \ln(V_C/V_D)}{T_h \ln(V_B/V_A)}$$

We can show that the ratio of the logarithmic quantities is 1 by establishing a relationship between the ratio of volumes. Using the Poisson relationship discussed in the previous chapter, we note that $TV^{\gamma-1} = constant$ for an adiabatic, quasi-static process. Applying this result to the adiabatic processes $B \rightarrow C$ and $D \rightarrow A$, we obtain

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1}$$
$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

Dividing the first equation by the second, we obtain

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Therefore, the Carnot efficiency is given by

$$e_C = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

If it were possible to have a reservoir at $T_c = 0$ temperature, we could create an ideal engine whose efficiency would be exactly one. In the other limit, if $T_c = T_h$, the efficiency is precisely zero.

The Carnot cycle, operating in a clockwise direction, had the net effect of removing energy from the high temperature reservoir and converting a portion of it into mechanical work, forming the Carnot engine. Now, we can think of operating the cycle in reverse, which would take energy in the form of heat from the low temperature reservoir and pass it on to the high temperature reservoir. This cycle forms the **Carnot refrigerator**. The efficiency of the refrigerator can be calculated from our earlier results and using the definition of efficiency for a refrigerator gives us

$$e_r = \left(\frac{Q_h}{Q_c} - 1\right)^{-1} = \left(\frac{T_h}{T_c} - 1\right)^{-1}$$

We see that because $T_h/T_c \geq 1$, the efficiency of the refrigerator becomes arbitrarily larger as $T_h \rightarrow T_c$, but it quickly becomes less than one when $T_h > 2T_c$. It's important to bear in mind what this results means: ***the work done to accomplish the transfer of energy from the low temperature reservoir to the high temperature reservoir will be less than the quantity of energy transferred in the form of heat*** provided that the temperature of the high temperature reservoir is less than twice the temperature of the low temperature reservoir.

3.5 Real Heat Engines

The previous section treated heat engines in an idealized way, arriving at the maximum theoretical limits. Here, we discuss how real heat engines operate. We choose three different cycles: (1) the Stirling cycle, (2) the Otto cycle, and (3) the Diesel cycle.

3.5.1 The Stirling Heat Engine
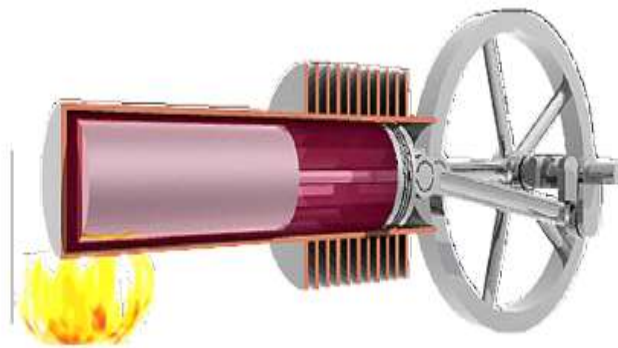
Figure 3.16 Schematic of the Stirling heat engine

The Stirling engine is a true, simple, practical heat engine that uses gas as its working substance and uses an external heat source. The engine consists of two cylinders with pistons, one in thermal contact with each reservoir. The pistons are connected to a crankshaft and between the two cylinders is a passageway where the gas flows past a **regenerator** – a temporary heat reservoir, typically made of wire mesh, whose temperature varies gradually from the hot side to the cold side. The gases used inside a Stirling engine never leave the engine. Because there are no exhaust valves or combustion processes, Stirling engines are very quiet. Today, Stirling engines are used in some very specialized applications, like in submarines or auxiliary power generators, where quiet operation is important. Because the Stirling engine is compatible with alternative and renewable energy sources it could become increasingly significant as the price of conventional fuels rises, and also in light of concerns such as peak oil and climate change.

The four steps of the engine's idealized cycle (known as a **Stirling cycle**) are as follows:

I. ***Power stroke***: While in the hot cylinder at temperature T_h, the gas absorbs heat and expands isothermally, pushing the hot piston outward. The piston in the cold cylinder remains at rest, all the way inward as shown in the figure.

II. ***Transfer to cold cylinder:*** The hot piston moves in while the cold piston moves out, transferring the gas to the cold cylinder at constant volume. While on its way, the gas flows past the regenerator, giving up heat and cooling to T_c.

III. ***Compression stroke***: The cold piston moves in, isothermally compressing the gas back to its original volume as the gas gives up heat to the cold reservoir. The hot piston remains at rest, all the way in.

IV. ***Transfer to hot cylinder***: The cold piston moves the rest of the way in while the hot piston moves out, transferring the gas back to the hot cylinder at constant volume. While on its way, the gas flows past the regenerator, absorbing heat unit it is again at T_h

It can be shown that the efficiency of the Stirling heat engine is given by

$$\frac{1}{e} = \frac{T_H}{T_H - T_C} + \frac{f}{2 \ln(V_2/V_1)}$$

Here f is the number of degrees of freedom per molecule.The Stirling engine is noted for high efficiency compared to steam engines, quiet operation, and its ability to use almost any heat source. The heat energy source is generated external to the Stirling engine rather than by internal combustion engines such as with the Otto cycle or Diesel cycle engines, which we discuss below. This engine is currently exciting interest as the core component of micro combined heat and power (CHP) units, in which it is more efficient and safer than a comparable steam engine. However, it has a low power-to-weight ratio rendering it more suitable for use in static installations where space and weight are not at a premium.

3.5.2 The Otto Cycle

Internal combustion engines are engines where the fuel is burned *inside* the engine cylinder as opposed to that where the fuel is burned *outside* the cylinder (e.g. the Stirling engine). Internal combustion engines are more economical than ideal-gas engines because a small engine can generate a considerable power. The thermodynamic cycle of an idealized internal combustion engine is called the **Otto cycle.**
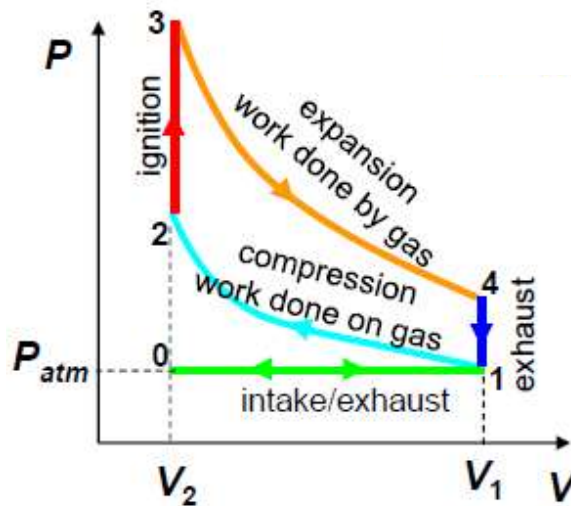
Figure 3.17 Schematic of the Otto cycle

As mentioned above, the Otto cycle is an idealized thermodynamic cycle which describes the function of a typical spark ignition gasoline engine. We consider the four stroke version of the Otto cycle as shown in Figure 3.17. The working substance is a mixture of air and fuel. The mixture is forced into a cylinder through one of two valves, which are built into the cylinder heat (at the top of the cylinder). The other valve is used to release waste gases from the cylinder at the appropriate point in the cycle. Also attached to the cylinder head is a spark plug, whose purpose it is to generate an electric spark when required. The base of the cylinder consists of a piston that is free to move up and down. The piston turns a crankshaft and a flywheel, which stores the mechanical energy that is transferred to it.

The Otto cycle officially begins during the **intake stroke**. For the intake stroke, the pressure is near atmospheric pressure and the gas volume is at a minimum. Next, the piston is pulled out of the cylinder with the intake valve open. The pressure remains constant during this stage, and the gas volume increases as fuel/air mixture is drawn into the cylinder through the intake valve. After the air-fuel mixture fills the cylinder, the intake valve is closed and the piston moves back into the cylinder in the **compression stroke**. During the compression stroke (from point "1" to "2"), the piston compresses the gas (almost) adiabatically, causing the gas volume to decrease and the pressure of the gas to increase (since work is done on the gas by the piston). When the piston is closest to the top of its motion, both valves remain closed and inside the cylinder, the air-fuel mixture is exploded by generating an electric spark. The explosion causes the pressure to rise very rapidly in the **ignition stroke**. We may model this by an isochoric process ("2" to "3") because the piston does not have time to move downward during the initial phase of the explosion.

Eventually, however, the hot gaseous products of the explosion expand, pushing the piston down in a more or less adiabatic process (from "3" to "4") in the **power stroke**, and the mechanical energy is transferred to the flywheel which stores it. When the piston reaches its lowest level, the exhaust valve opens and the (cooler) products of the combustion are released into the atmosphere as the piston continues moving upward in the so-called **exhaust stroke**. When it has reached top dead center again, the exhaust valve is closed and the intake valve is opened to let in a fresh batch of the air-fuel mixture as the piston makes its way down again. Both these steps can be represented by the isochoric process from "4" to "1". The intake valve is closed when the piston reaches the bottom and, with both valves now closed, the air fuel mixture is compressed adiabatically until the piston returns to top dead center, when the cycle is complete and ready to be repeated.

In our idealized version of events, energy in the form of heat is absorbed by the engine during the second stage, and rejected by the engine during the fourth stage. Both these processes are isochoric, the first being at the smallest possible volume, V_1, in the cylinder and the last being at the largest possible volume, V_2. The ratio $b = V_2/V_1$ is generally called the **compression ratio** and expresses the degree to which the air-fuel mixture is compressed before ignition. The work done by the cycle is

$$W = -K_{12} \int_{V_1}^{V_2} V^{-\gamma}\, dV - K_{34} \int_{V_2}^{V_1} V^{-\gamma}\, dV$$

where we use the adiabatic equation of state for the two adiabatic stages that do work and the subscript on K refers to the path. Using the ideal gas law, it can be shown that

$$W = \frac{Nk}{\gamma - 1}(T_3 - T_4 + T_1 - T_2)$$

On the other hand, heat is absorbed during an ignition stroke and therefore

$$Q_h = U_3 - U_2 = C_V(T_3 - T_2)$$

so the efficiency of the engine is

$$e_{otto} = \frac{Nk}{C_V(\gamma - 1)}\left(1 - \frac{T_4 - T_1}{T_3 - T_2}\right)$$

It can be shown that the ratio of the temperatures in the square brackets can be given in terms of the compression ratio so that the efficiency of the Otto cycle is given in terms of the compression ratio:

$$e_{otto} = 1 - b^{1-\gamma}$$

Clearly, $0 < e_{otto} < 1$ because $\gamma > 1$ as we have seen. Note that the efficiency of the idealized Otto cycle depends only on the compression ratio; the larger the compression ratio the greater the efficiency. However, in practice, it is not possible to increase the compression ratio indefinitely because one is limited by the volatility of the air-fuel mixture. Excessive compression ratios can cause the mixture to burn prematurely, i.e., before the spark ignites it at top dead center. This will cause the engine to actually lose power and efficiency.

3.5.3 The Diesel Cycle

The difference between the Otto cycle and the Diesel cycle is that the fuel mixture is not ignited suddenly by a spark, but is ignited by the higher compression and is then allowed to burn slowly. In the Diesel cycle, auto-ignition occurs due to compression and thus heat transfer occurs at constant pressure. A schematic of the diesel engine is given below.
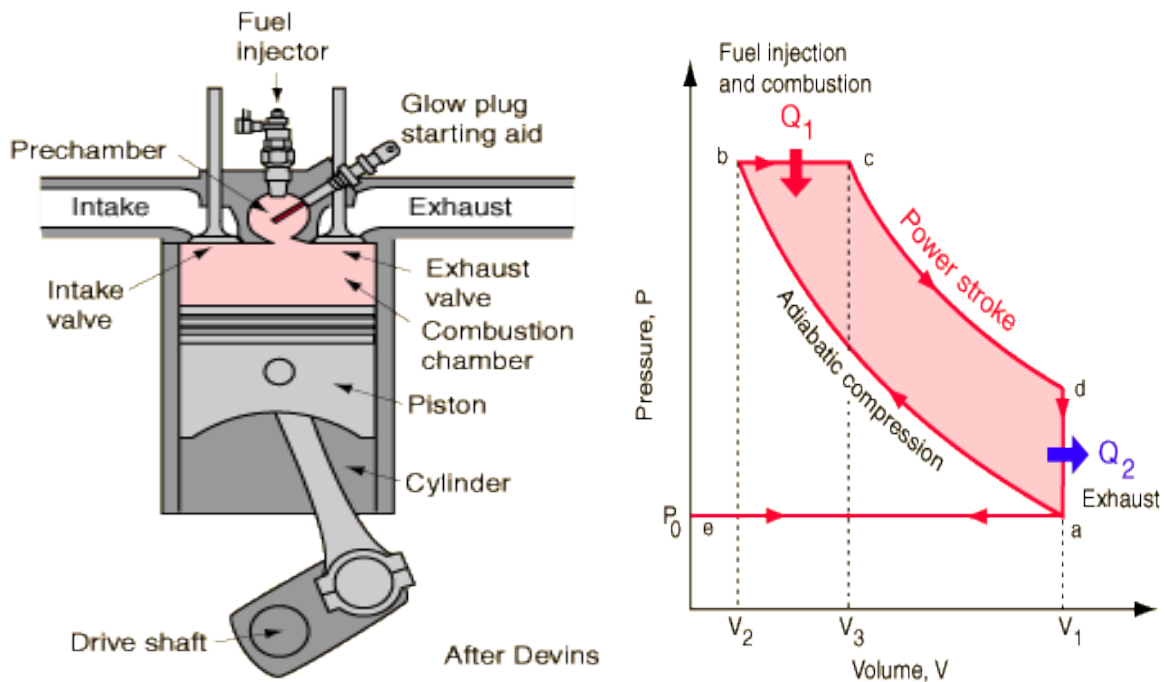
Figure 3.18 Schematic of the Diesel engine and its corresponding Diesel cycle

81

In Figure 3.18, the burning begins at the compressed volume V_2. The gas then expands pushing the piston down in the power stroke which occurs through two stages, first in an isobaric process to volume V_3 as the fuel continues to burn and then in an adiabatic process (the same as the power stroke for the idealized Otto cycle) when the fuel is spent to volume V_1. The exhaust stroke occurs when the exhaust valve is opened and the waste gases are eliminated. A fresh batch of the air-fuel mixture is let into the combustion chamber during the intake stroke and compressed during the compression stroke in last stage, bringing the cycle to completion.

The efficiency is slightly more difficult to calculate than for the Otto cycle, because work is now done in three of the four stages and energy in the form of heat is absorbed during an isobaric process. The heat input and output of the engine is given by

$$Q_h = C_p(T_c - T_b), \quad Q_c = C_V(T_d - T_a)$$

so the efficiency of the cycle is

$$e_{diesel} = 1 + \frac{1}{\gamma}\frac{T_a - T_d}{T_c - T_b}$$

Similar to the Otto cycle, the ratio of the temperatures can be given in terms of the compression ratio so that the efficiency of the Diesel cycle is given in terms of the **compression ratio** $b = V_1/V_2$ and the **cut-off ratio** $c = V_3/V_2$. Thus, it can be shown that the efficiency of the Diesel cycle is given by

$$e_{diesel} = 1 - \frac{b^{1-\gamma}(c^\gamma - 1)}{\gamma(c - 1)}$$

Because there is no spark and the fuel burning is slow, the Diesel cycle is less stressful on the engine than the Otto cycle. For this reason, diesel engines tend to last longer and cost less to maintain than gasoline engines.

In the next chapter, we will use the insights developed from the Carnot theorem to give a precise definition of entropy and to introduce the modern statement of the second law.

Chapter 4: Entropy and the 2nd Law

The last chapter demonstrated that the second law of thermodynamics restricts that development of any type of perpetual motion machine. However, perpetual motion machines are not the only processes that never seem to occur in nature. A little thought will show that in fact there are many processes that do not occur spontaneously in nature even though the first law would allow them. For example, a lake on a warm summer's day does not simply give up its energy to the atmosphere and freeze, although energy would be conserved in the process. More generally, if two bodies, *A* and *B*, at temperatures T_A and T_B with $T_A \geq T_B$ are placed in thermal contact, it never happens that *A* spontaneously keeps getting hotter and *B* colder. An egg that has been dropped and splattered on the floor does not spontaneously put itself together again even though such a process may not in fact violate energy conservation. An isolated gas does not undergo spontaneous compression in a vacuum, even though such a process may not violate energy conservation. The impossibility of the processes described in the examples above is captured by the **second law of thermodynamics**.

The next step in our development of the second law will be the concept of **entropy** in thermodynamics. This is the precursor of the definition of **information**. Information is carried, stored and processed by all macroscopic physical systems and is ultimately governed by the laws of physics, so it is not surprising that physics and information should be closely related to one another. The usefulness of the concept of entropy can hardly be overstated and it is probably fair to say that the connection between physics and information is still not fully exploited. We will look at the microscopic origins of the entropy in future chapters; for now we introduce it as a thermodynamic state variable. In this chapter, we will introduce the concept of entropy, a concept that provides us with the most modern statement of the second law of thermodynamics and has a good claim for being one of the deepest ideas in all of physics.

4.1 Introduction to Entropy

Let us consider an arbitrary reversible thermodynamic cycle, *S*, and divide the cycle into a large number of Carnot engines as shown in Figure 4.1. This procedure is qualitatively similar to using a collection of Riemann sums to determine the integral of a given function. An important property of each of the Carnot cycles is that heat is absorbed and rejected by the cycle during isothermal processes and thus, we can write

$$\frac{Q_{in}}{T_{in}} - \frac{|Q_{out}|}{T_{out}} = 0$$
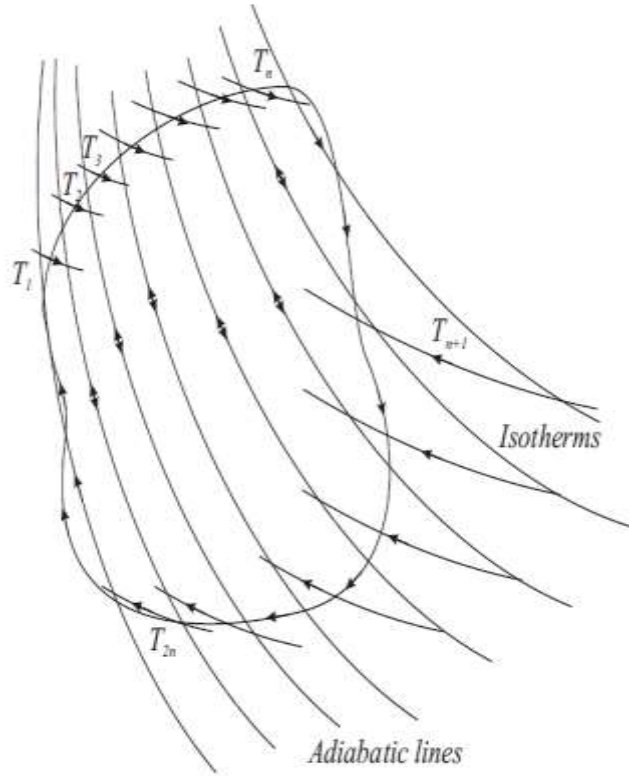
Figure 4.1 A schematic of an arbitrary reversible cycle in thermodynamic phase space

Each of the Carnot cycles in the figure absorbs and rejects an infinitesimal quantity of energy as heat, δQ_i, at each reservoir. Moreover, the reservoirs come in pairs, so let's label them *1* to *2n* in such a way that the Carnot cycle *j* operates between temperatures T_j (high) and T_{n+j} (low), where *n* represents the number of cycles. For the set of cycles shown in Figure 4.1, we can say that

$$\sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = 0 \quad (4.1)$$

As the series of Carnot cycles exactly reproduce the original cycle, the number of cycles approach infinity and thus the adiabats become infinitesimally close to each other. Therefore δQ_i approaches zero at each reservoir, and thus, we have

$$\lim_{n \to \infty} \sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = \oint_S \frac{\delta Q}{T} = 0$$

Let's consider the implications of this statement. Because

$$\oint_S \frac{\delta Q}{T} = 0$$

for a reversible cycle, then the differential $\delta Q/T$ must be exact and thus its integral must be independent of the path taken in thermodynamic phase space. This implies that *during a reversible process*, there exists a state function, S, such that

$$\delta Q = T \, dS \Rightarrow \Delta S = \int_{i,(q.s.)}^{f} \frac{\delta Q}{T} \qquad (4.2)$$

where we have introduced the suffix "q.s." to emphasize the fact that the integral is to be evaluated along some reversible, quasi-static path from i to f. Note that no further specification of the path is required since, so long as the path is quasi-static, the change $\Delta S = S_f - S_i$ will be the same. The function S is called the **entropy** of the system.

Equation (4.2) tells us how to compute changes in the entropy of a system that has been transformed from a state i to a state f, but tells us nothing of the actual value of the entropy at i or f or anywhere else. However, imagine that we choose a standard state, call it *, at which we arbitrarily set the entropy to be numerically equal to zero (like potential energy in classical mechanics, only changes in entropy are relevant), then

$$S(k) = \int_{*}^{k} \frac{\delta Q}{T}$$

gives the entropy of any other state, k. A change in our standard would simply introduce a constant; thus, we can write the entropy of any state k as the indefinite integral

$$S(k) = \int^{k} \frac{\delta Q}{T} + S_*$$

with an arbitrary constant, S_*.

4.2 Entropy for Irreversible Cycles

Now consider an irreversible cycle. This implies that there are one or more portions of the cycle that cannot be accurately described by Carnot cycles as depicted in Figure 4.1.

Consider one such portion, which we will label k, and let's call the actual energy absorbed as heat at the high temperature reservoir involved in covering this portion $\delta Q'_k$ and the actual energy rejected as heat at the low temperature reservoir $\delta Q'_{k+n}$. From the Carnot theorem, we know that

$$1 - \frac{|\delta Q'_{k+n}|}{\delta Q'_k} \leq 1 - \frac{|\delta Q_{k+n}|}{\delta Q_k} \Rightarrow \frac{|\delta Q'_{k+n}|}{\delta Q'_k} \geq \frac{|\delta Q_{k+n}|}{\delta Q_k} \Rightarrow \frac{\delta Q'_k}{|\delta Q'_{k+n}|} \leq \frac{\delta Q_k}{|\delta Q_{k+n}|} = \frac{T_k}{T_{k+n}}$$

Therefore, we have

$$\frac{\delta Q'_k}{T_k} - \frac{|\delta Q'_{k+n}|}{T_{k+n}} \leq 0$$

To reproduce the cycle, the sum on the left of Equation (4.1) should be replaced by

$$\sum_{i=1}^{'2n} \frac{\delta Q_i}{T_i} + \sum_k \left(\frac{\delta Q'_k}{T_k} - \frac{|\delta Q'_{k+n}|}{T_{k+n}} \right)$$

where the prime on the first sum on the right indicates that those Carnot cycles overlapping portions of the cycle that are not reversible should be omitted and replaced by the second sum on the right. Since the first sum above is identically zero and the second sum is less than or equal to zero, we have

$$\sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} \leq 0$$

and in the limit as the number of adiabatic lines approaches infinity,

$$\lim_{n \to \infty} \sum_{i=1}^{2n} \frac{\delta Q_i}{T_i} = \oint_S \frac{\delta Q}{T} \leq 0$$

The equality holds only when S is reversible.

To examine implications of this statement, suppose that we have an isolated thermodynamic system that goes through an irreversible process, as shown in Figure 4.2. Let's choose two points on the cycle so that path I from i to f is not quasi-static and path II from f to i is quasi-static. Then

$$\oint_S \frac{\delta Q}{T} \leq 0 \Rightarrow \int_{I,i}^{f} \frac{\delta Q}{T} \leq \int_{II,i}^{f} \frac{\delta Q}{T}$$

Now, by definition, because path *II* is quasi-static, then

$$\int_{II,i}^{f} \frac{\delta Q}{T} = S_f - S_i \Rightarrow \Delta S \geq \int_{I,i}^{f} \frac{\delta Q}{T} \quad (4.3)$$
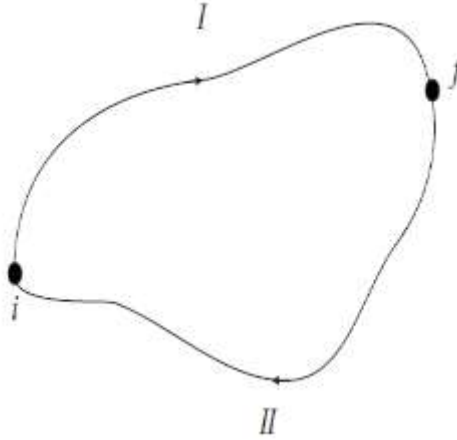
Figure 4.2 A schematic of an irreversible cycle

In particular, since path *I* is not restricted to be quasi-static, we could take it to be adiabatic and thus $\delta Q = 0$. Therefore, we find that $\Delta S \geq 0$. This is a profoundly important statement, which is worth repeating:

The entropy of a thermally isolated system undergoing any thermodynamic process may never decrease

This is the most modern statement of the second law of thermodynamics. Moreover, it follows that ***thermally isolated systems achieve equilibrium at the maximum of the entropy***, but it is essential to keep in mind that this holds only for thermally isolated systems.

If we examine the change of entropy of a system and its immediate surroundings, the entropy of the system may decrease; however, the entropy of the universe (defined as the system and its surroundings) must either increase or remain the same. As a simple example, consider the earth-sun system as reasonably isolated, and only that part of the energy from the sun that is incident upon the earth, ignoring the rest. To a very good approximation both the sun and the

earth can be approximated by reservoirs at temperatures T_s and T_e. The net change in entropy of the system when δQ of energy from the sun is absorbed by the earth as heat is

$$\Delta S = -\frac{\delta Q}{T_s} + \frac{\delta Q}{T_e} > 0$$

since $T_e \ll T_s$.

Equation (4.3) also gives us the general expression for entropy which also applies to irreversible processes $\delta Q \leq T \, dS$ so, in terms of the entropy, the first law of thermodynamics reads

$$T \, dS \geq dU + PdV$$

or more generally,

$$T \, dS \geq dU + \sum_i P_{X_i} dX_i$$

This statement and the statement that $\Delta S \geq 0$ for an isolated system together summarize the content of the first two laws of thermodynamics. If attention is confined exclusively to processes are reversible, we have

$$dU = TdS - \sum_i P_{X_i} dX_i \quad (4.4)$$

with $\Delta S = 0$. Equation (4.4) is known as a **thermodynamic identity** and is called **Gibbs equation**.

4.3 Entropy and Heat Engines

We can use the definition of entropy to discuss the problem that motivated the development of thermodynamics – the efficiency of heat engines. We know that an engine converts energy from a heat source to work and returns to its initial state. According to Equation (4.2), the transfer of energy from a heat source lowers the entropy of the source. If the energy transferred is used to do work, the work done must be done on some other system. Because the process of doing this work may be quasi-static and adiabatic, the work done need not involve a change of entropy. However, if all of the energy transferred were converted into work, the total entropy would decrease, and thus, we would violate the entropy statement of the second law.

Therefore, we arrive at the conclusion summarized in the Kelvin-Planck statement of the second law: no process is possible whose sole result is the complete conversion of energy into work.

To show that the entropy statement of the second law also implies the Carnot theorem, let's calculate the entropy associated with the Carnot engine. In the Carnot cycle, the high temperature reservoir transfer energy Q_h to the engine and the engine does work W and transfers energy Q_c to the heat sink. Since the Carnot engine is reversible, the internal energy and entropy of the engine remain unchanged. From the entropy statement of the second law, we have

$$\Delta S_{TOTAL} = \Delta S_h + \Delta S_c = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

Upon rearranging, we have

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h} \qquad (4.5)$$

Since the Carnot efficiency is given by $e = 1 - T_c/T_h$, this implies that the engine is most efficient when the ratio Q_l/Q_h is as small as possible. However, Equation (4.5) shows that Q_c/Q_h is a minimum when the cycle is reversible or when $\Delta S = 0$. Therefore, the entropy statement of the second law constrains the maximum thermal efficiency of all engines to be the Carnot efficiency. Moreover, since the Carnot cycle is reversible, this also implies that the second law constrains the maximum thermal efficiency of all refrigerators to be the Carnot efficiency. This implies work must be done on a refrigerator in order for heat to be transferred from a cold temperature reservoir to a warm reservoir. Therefore, we arrive at the conclusion summarized in the Clausius statement of the second law: no process is possible whose sole result is the transfer of heat from a cold body to a warm body.

As mentioned in the introduction, perpetual motion machines cannot exist due to limitations of the laws of thermodynamics. Perpetual motion machines of the first type seek to create the energy required for their operation out of nothing, which is a violation of the first law of thermodynamics. However, perpetual motion machines of the second type attempt to convert all energy into useful work. Thus, perpetual motion machines of the second type seek to extract the energy required for their operation in a manner that decreases the entropy of an isolated system, which is a violation of the second law of thermodynamics.

The second law suggests that *the fundamental difference between transferring purely mechanical energy (i.e. work) and transferring heat is the difference in the entropy transfer*. Transferring purely mechanical energy to or from a system does not necessarily change its entropy (since $\Delta S = 0$ for reversible processes). For this reason, all forms of work are

thermodynamically equivalent to each other – they are freely convertible into each other, and in particular, into mechanical work. Work can be completely converted into heat, but the inverse is not true. The transfer of energy by heat is *always* accompanied with the entropy transfer $dS = \delta Q/T$. Based on the laws of thermodynamics, we have two important realities for heat engines:

1. First, entropy enters the system with heating, but does not leave the system with the work.
2. On the other hand, for a continuous operation of a heat engine, ***the net entropy change during a cycle must be zero*** since it is a state function.

How is this accomplished?
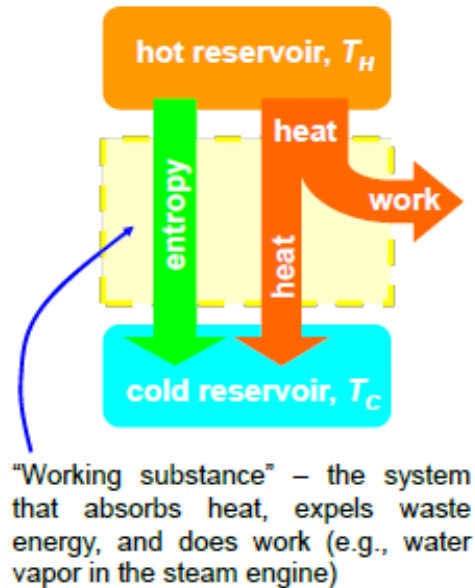
Figure 4.3 Entropy transfer for heat engines

An engine can get rid of *all* the entropy received from the hot reservoir by transferring only *part* of the input thermal energy to the cold reservoir, as shown in Figure 4.3. Thus, the only way to get rid of the accumulating entropy is to absorb more internal energy in the heating process than the amount converted to work, and to "flush" the entropy with the flow of the waste heat out of the system. Thus, an essential ingredient of all heat engines is the temperature difference between hot and cold reservoir. Thus, there are three basic consequences of this process:

1. Any difference $T_H - T_C \geq 0$ can be exploited to generate mechanical energy.
2. The greater the temperature difference, the more efficient the engine.

3. Energy waste is inevitable.

Real heat engines have lower efficiencies because the processes within the devices are not perfectly reversible – the entropy will be generated by irreversible processes. Some sources of irreversibility include

1. Heat may flow directly between reservoirs
2. Not all temperature difference may be available (temperature drop across thermal resistances in the path of the heat flow)
3. Part of the work generated may be converted to heat by friction
4. Gas may expand irreversibly without doing work (as gas flow into vacuum)

4.4 Entropy, Temperature, and Pressure

In this section, we will show how the temperature and pressure can be defined in terms of the entropy. In doing so, we will develop a more general reliable definition of these thermodynamic variables, which will be called the **thermodynamic temperature** and **thermodynamic pressure**.

4.4.1 Thermodynamic Temperature

We previously showed that the qualitative definition of temperature follows by considering the condition for the thermal equilibrium of two thermodynamic systems in thermal contact. Moreover, our operational definition of temperature scales was based on an empirical extrapolation from the ideal gas law. Now that we have the definition of entropy, we can give a more general and precise view of temperature that is independent of the thermodynamic system.
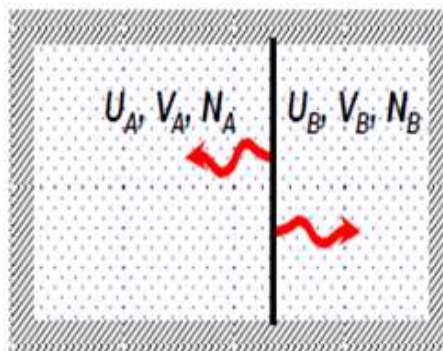
Figure 4.4 Schematic of an isolated composite system that is partitioned into two subsystems

Consider an isolated composite system that is partitioned into two *subsystems A* and *B* by a fixed, impermeable, insulating wall. For the composite system, we have

$$U = U_A + U_B = const., \quad V = V_A + V_B = const., \quad N = N_A + N_B = const.$$

Because the entropy is additive, we can write the total entropy as

$$S = S_A(U_A, V_A, N_A) + S_B(U_B, V_B, N_B)$$

For thermal equilibrium to be established, we replace the fixed, impermeable, *insulating* wall by a fixed, impermeable, *conducting* wall so that the two subsystems are in thermal contact and energy transfer by heating and cooling may occur. According to the second law of thermodynamics, the values of U_A and U_B will change in such a way that the entropy of the composite system becomes a maximum. To find the value of U_A that maximizes S, we calculate

$$dS = \left(\frac{\partial S_A}{\partial U_A}\right) dU_A + \left(\frac{\partial S_B}{\partial U_B}\right) dU_B = 0$$

Because the total internal energy of the system is conserved, we have $dU_B = -dU_A$, and hence

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

Because the temperatures of the two systems are equal in thermal equilibrium, we conclude that the derivative $\partial S/\partial U$ must be associated with the temperature. Therefore, using dimensional analysis, we define the **thermodynamic temperature** as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad (4.6)$$

which implies that the condition for thermal equilibrium is

$$\frac{1}{T_A} = \frac{1}{T_B} \Rightarrow T_A = T_B$$

Based on the above analysis, the temperature can be interpreted as the response of the entropy to a change in the internal energy of the system.

In our derivation, we have found that, if two systems are separated by a conducting wall, energy will be transferred until the systems reach the same temperature. Now suppose that the two systems are initially separated by an insulating wall and that the temperatures of the two systems are almost equal with $T_A > T_B$. If this constraint is removed, we know that energy will be transferred across the conducting wall and the entropy of the composite system will increase. The change in entropy of the composite system is

$$\Delta S \approx \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta U_A > 0$$

where T_A and T_B are the initial values of the temperatures. The condition that $T_A > T_B$ requires that $\Delta U_A < 0$ in order for $\Delta S > 0$. Therefore, we conclude that the definition of the thermodynamic temperature implies that energy is transferred from a system with a higher value of T to a system with a lower value of T. This is a restatement of the Clausius statement of the second law: **No process exists in which a cold body becomes cooler while a hotter body becomes still hotter while the constraints on the bodies and the state of its environments remain unchanged**.

When a high temperature object is placed in contact with a low temperature object, then energy will flow from the high temperature object to the lower temperature object, and they will approach an equilibrium temperature. When the details of this common-sense scenario are examined, it becomes evident that the simple view of temperature embodied in the commonly used kinetic theory approach to temperature has some significant problems.
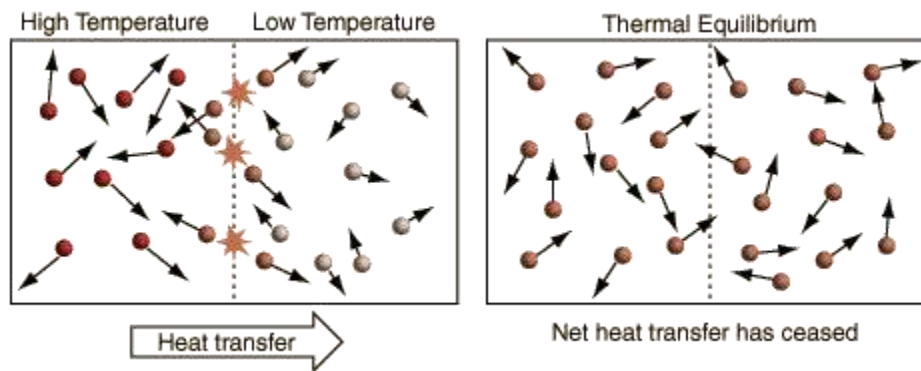
Figure 4.5 Schematic of energy exchange via kinetic theory

The above illustration summarizes the situation when the kinetic theory view of temperature gives a reasonable general description of the nature of temperature. For monatomic gases acting like point masses, the kinetic theory view of temperature gives a reasonable general description of the nature of temperature. For monatomic gases acting like point masses, a higher temperature simply implies higher average kinetic energy. Faster molecules striking slower ones

at the boundary in elastic collisions will increase the velocity of the slower ones and decrease the velocity of the faster ones, transferring energy from the higher temperature to the lower temperature region. With time, the molecules in the two regions approach the same average kinetic energy (same temperature) and in this condition of thermal equilibrium there is no longer any net transfer of energy from one object to the other.

The concept of temperature is complicated by internal degrees of freedom like molecular rotation and vibration and by the existence of internal interactions in solid materials which can include collective modes. The internal motions of molecules affect the specific heats of gases, with diatomic hydrogen being the classic case (as in Figure 4.6). Collective modes affect the specific heats of solids, particularly at low temperatures. Complications such as these have led to the adoption of a different approach to the concept of temperature in the study of thermodynamics. Since changes in internal energy are associated with heat exchange between the system and its environment during an isochoric process, we can produce a more general, reliable, and theoretical definition of temperature.

Temperature is a measure of the tendency of an object to spontaneously give up energy to its surroundings. When two objects are in thermal contact, the one that tends to spontaneously lose energy is at the higher temperature.
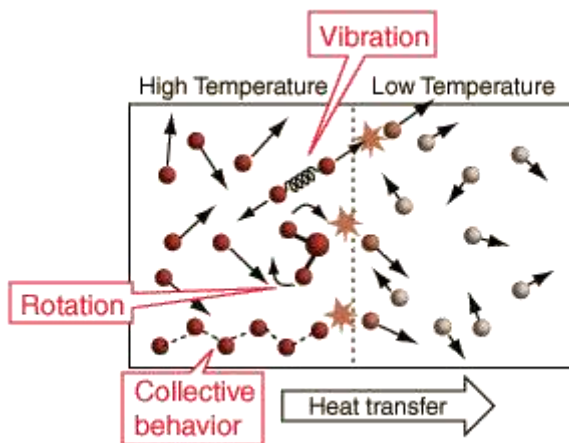
Figure 4.6 Schematic of energy exchange including internal degrees of freedom

4.4.2 Thermodynamic Pressure

In the previous section, we showed that the thermodynamic definition of temperature follows by considering the condition for the thermal equilibrium of two subsystems. By

definition, we say that two systems in contact with one another are in **mechanical equilibrium** when their pressures are equal. In the following, we show that the pressure can be defined in an analogous way by considering the condition for the mechanical equilibrium of two subsystems.

As before, consider an isolated system that is partitioned into two subsystems, as in Figure 4.4. The subsystems are separated by a movable, insulating wall so that the energies and volumes of the subsystems can adjust themselves, but N_A and N_B (the number of molecules in each subsystem, respectively) are fixed. For simplicity, we assume that U_A and U_B have already changed so that thermal equilibrium has been established. For fixed total volume V, we have one independent variable, which we take to be V_A; V_B is given by $V_B = V - V_A$. The value of V_A that maximizes $S = S_A + S_B$ is given by

$$dS = \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B = 0$$

Since $dV_A = -dV_B$, then the condition for mechanical equilibrium can be written as
$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

Because the pressure of the two systems is equal in mechanical equilibrium, we conclude that the derivative $\partial S/\partial V$ must be associated with the pressure. Therefore, using dimensional analysis, we define the **thermodynamic pressure** as

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \qquad (4.7)$$

This expression states that the pressure can be interpreted as the response of the entropy to a change in the volume of the system. Since heat exchange between a system and its environment is caused by work done by the working substance, the above expression states that pressure can be defined as the change in entropy of a thermodynamic system in response to work done by the system. Thus, a system with high (low) pressure is associated with significant (small) heat exchange in response to compression/expansion

Note that Equation (4.7) implies the increase of volume corresponds to an increase of entropy. Thus, increases in entropy correspond to pressure decreases and other irreversible changes in a system. This suggests that entropy can be considered as a measure of energy concentration. Thus, if the same amount of energy disperses into a larger volume, the entropy must increase.

Now suppose that the two systems are initially separated by a fixed, insulating wall and that the pressures of the two systems are almost equal with $P_A > P_B$. If this constraint is removed by replacing it with a movable, insulating wall, we know that energy will be transferred across through the wall (via work) and the entropy of the composite system will increase. As the system approaches mechanical equilibrium, the change of entropy of the composite system will increase

$$\Delta S \approx \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\Delta V_A > 0$$

If $P_A > P_B$, then $\Delta V_A > 0$, which implies that volume is transferred from a system with a low value of P to a system with a higher value of P. Thus, no process exists in which a body at higher pressure contracts while a body at lower pressure expands while the constraints on the bodies and the state of its environments remain unchanged. ***Pressure is a measure of the tendency of an object to spontaneously expand in its surroundings.***

4.5 Entropy and Diffusion

Just as heat conduction is the transport of energy by random thermal motions, diffusion is the transport of particles by random thermal motion. Moreover, like the flow of energy, the flow of particles by diffusion obeys an equation that is fairly easy to predict. Just as heat conduction is caused by a temperature difference, diffusion is caused by a difference in the *concentration* of particles n.
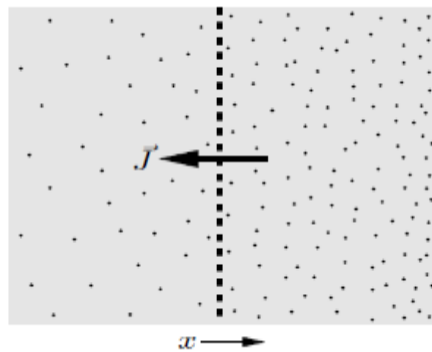
Figure 4.7 Schematic of energy exchange including internal degrees of freedom

Suppose we have a region where the parcel concentration increases uniformly in the x direction. The flux $\vec{J}$ of these particles across any surface is the net number of particles that cross this surface per unit time. Experimentation shows that flux of particles across any surface is proportional to the concentration gradient

$$J_x = -D\frac{dn}{dx}$$

This equation is known as **Fick's law**, after the 19th century German physiologist Adolf Eugen Fick. The minus sign indicates that diffusion is always directed from regions of high concentration to low concentration (i.e. in the direction to reduce the gradient). The constant D is known as the diffusion coefficient.
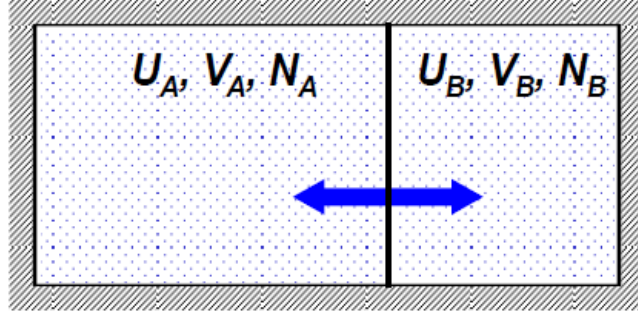
Figure 4.8 Schematic of an isolated composite system that is partitioned into two subsystems with a fixed, permeable wall

Just as entropy defines the direction of spontaneous energy flow, entropy defines the direction of spontaneous particle flow. Consider an isolated system that is partitioned into two subsystems, as in Figure 4.8. The subsystems are separated by a fixed, insulating, permeable membrane so that the internal energy and the volume of each subsystem is fixed, but N_A and N_B can adjust themselves. For simplicity, we assume that U_A and U_B have already changed so that thermal equilibrium has been established and that P_A and P_B have already changed so that mechanical equilibrium has been established. For fixed total number of particles N, we have one independent variable, which we take to be N_A; N_B is given by $N_B = N - N_A$. If we allow the system to evolve over a long time period, the net flux of particles will eventually cease and the system will reach equilibrium − a condition known as **diffusive equilibrium**. The value of N_A that maximizes $S = S_A + S_B$ is given by

$$dS = \frac{\partial S_A}{\partial N_A}dN_A + \frac{\partial S_B}{\partial N_B}dN_B = 0$$

Since the total number of particles is fixed of the system is conserved, then $dN_A = -dN_B$ and we have

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

We conclude that the derivative $\partial S/\partial N$ must be associated with the properties of diffusion. We will now define a quantity known as the **chemical potential** denoted μ:

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \qquad (4.8)$$

Just as the temperature is the same when two systems are in thermal equilibrium and the pressure is the same when two systems are in mechanical equilibrium, the chemical potential is the quantity that is the same when two systems are in diffusive equilibrium. If two systems are not in equilibrium, then the one with the larger value of $\partial S/\partial N$ will tend to gain particle (since it will thereby gain more entropy than it loses). Because of the definition of chemical potential, this system has the *smaller* value of μ. As a conclusion, ***particles tend to flow from the system with higher μ into the system with lower μ.***

Note that Equation (4.8) implies that the increase of number density corresponds to a decrease in entropy. Thus, increases in entropy correspond to decreases of chemical potential and other irreversible changes in a system. This suggests that entropy can be considered as a measure of particle concentration. Thus, if the same amount of particles disperses into a larger volume, the entropy must increase.

Returning to the previous example in Figure 4.8, we can see that as the system approaches equilibrium, the change of entropy of the composite system will increase

$$\Delta S \approx - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) \Delta N_A > 0$$

If $\mu_A > \mu_B$, then $\Delta N_A < 0$, which implies that particles flow spontaneously from higher chemical potential to lower chemical potential. Thus, no process exists in which the particle concentration spontaneously increases while the constraints on the bodies and the state of its environments remain unchanged. This means the entropy provides a constraint for energy flow and particle flow. Based on these considerations, we can describe chemical potential as ***a measure of the tendency of an object to spontaneously diffuse particles in its surroundings.***

4.6 Entropy Changes in Irreversible Processes

As we have already seen, the key to thermodynamics is understanding the role of entropy changes. By definition, calculation of the change in entropy requires information about a reversible path connecting the initial and final equilibrium states. To calculate changes in entropy for real (irreversible) processes, we must remember that entropy (like internal energy) is a state function and thus, depends only on the state of the system. Hence, the change in entropy when a

system moves between any two equilibrium states depends only on the initial and final states. We can show that if this were not the case, the second law of thermodynamics would be violated

We now calculate the entropy change in some irreversible process between two equilibrium states by devising a reversible process (or series of reversible processes) between the same two states and computing ΔS for the reversible process. In reversible processes, it is critically important that we distinguish between Q, the actual energy transfer in the process, and Q_r, the energy that would have been transferred by heat along a reversible path. Only Q_r is the correct value to be used in calculating the entropy change. In this section we apply the techniques of thermodynamics to calculating entropy changes to a variety of macroscopic systems.

Example 1: Entropy Change in a Free Expansion
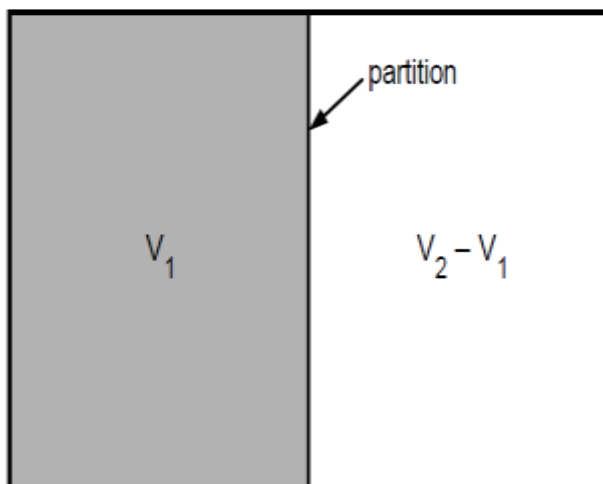
Figure 4.8 Spontaneous expansion into a vacuum

Consider an ideal gas in a closed, insulated container divided into two chambers by an impermeable partition, as in Figure 4.8. The volume of one chamber is V_1 and that of the two chambers taken together is V_2. To compute the entropy change in the universe, we will use Gibbs equation (4.4) which states that

$$dU = TdS - PdV \Rightarrow dS = \frac{dU}{T} + \frac{P}{T}dV$$

Since there is no temperature change in the gas, we have

$$dS = \frac{P}{T}dV = \frac{Nk}{V}dV \Rightarrow \Delta S = Nk \ln\left(\frac{V_2}{V_1}\right)$$

In this process, the entropy of the universe increased even though there was no change in internal energy of the system, consistent with the second law of thermodynamics. To restore the gas to its original state requires work

$$\delta W = -P\, dV = -NkT\frac{dV}{V} \Rightarrow W = Nk \ln\left(\frac{V_2}{V_1}\right) = T\Delta S$$

In this calculation, it is assumed that the compression of the gas is carried out at a constant temperature T. This simple example demonstrates that the spontaneous expansion of a thermally isolated ideal gas is a consequence of the second law, whereas the spontaneous compression of a thermally isolated gas is a violation of the second law. This illustrates that the free expansion of an ideal gas is also an irreversible process.

Example 2: Entropy Change due to Thermal Contact
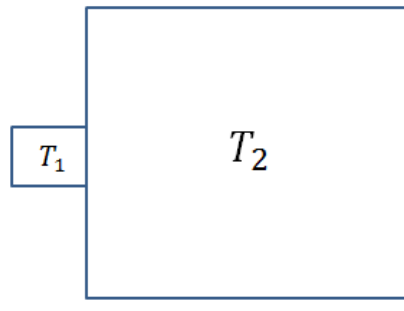
Figure 4.9 Heating or cooling of an ideal gas

Let's consider the heating or cooling of an ideal gas, as in Figure 4.9. For simplicity, we take a fixed volume of gas in contact with a much larger volume of the same gas. The two volumes are insulated from their surroundings. Initially, the temperature of the small volume is T_1, and that of the large volume is $T_2 > T_1$. During the passage of time, both volumes come to the same equilibrium temperature T. In this process, total internal energy is conserved so that we can determine the equilibrium temperatures

$$C_{V,1}T_1 + C_{V,2}T_2 = (C_{V,1} + C_{V,2})T \Rightarrow T = \frac{C_{V,1}T_1 + C_{V,2}T_2}{C_{V,1} + C_{V,2}} \qquad (4.9)$$

The volume does not change in this process, and hence the change in entropy is

$$dS_{TOTAL} = dS_1 + dS_2 = \frac{dU_1}{T} + \frac{dU_2}{T_2} = C_{V,1}\frac{dT}{T} + C_{V,2}\frac{dT}{T} \Rightarrow \Delta S = C_{V,1} \ln\left(\frac{T}{T_1}\right) + C_{V,2} \ln\left(\frac{T}{T_2}\right)$$

Let's consider the limiting case of an infinite reservoir, which requires us to determine ΔS as $C_{V,1}/C_{V,2} \to 0$. Let's define the ratio $\lambda = C_{V,1}/C_{V,2}$ and rewrite (4.9) in terms of λ as

$$T = \frac{C_{V,1}}{C_{V,1} + C_{V,2}} T_1 + \frac{C_{V,2}}{C_{V,1} + C_{V,2}} T_2 = \frac{1}{1 + \lambda}(\lambda T_1 + T_2)$$

The total change in entropy is given by

$$\Delta S_{TOTAL} = \Delta S_1 + \Delta S_2 = C_{V,1} \ln\left(\frac{T}{T_1}\right) + C_{V,2} \ln\left(\frac{T}{T_2}\right) \qquad (4.10)$$

In the limit $\lambda \to 0$, which corresponding to system 2 becoming a heat reservoir, we see from (4.10) that $T = T_2$. Thus, the first term in (4.10) gives

$$\Delta S_1 = C_{V,1} \ln\left(\frac{T}{T_1}\right) \to C_{V,1} \ln(T_2/T_1)$$

in the limit that system 2 is treated as a heat reservoir. To evaluate the second term in (4.10), we write

$$\frac{T}{T_2} = \frac{1}{1 + \lambda}\left(1 + \lambda \frac{T_1}{T_2}\right) \approx (1 - \lambda)\left(1 + \lambda \frac{T_1}{T_2}\right) \approx 1 + \lambda\left(\frac{T_1}{T_2} - 1\right)$$

where we have used the approximation $(1 + x)^{-1} \approx 1 - x$, and kept terms through order λ.

Therefore, we have

$$\Delta S_2 = C_{V,2} \ln\left(\frac{T}{T_2}\right) \to \frac{C_{V,1}}{\lambda} \ln\left[1 + \lambda\left(\frac{T_1}{T_2} - 1\right)\right] \approx \frac{C_{V,1}}{\lambda}\left[\lambda\left(\frac{T_1}{T_2} - 1\right)\right] = C_{V,1}\left(\frac{T_1}{T_2} - 1\right)$$

\noindent where we have used the approximation $\ln(1 + x) \approx x$. Hence, the total change in the entropy of the system is given by

$$\Delta S = C_{V,1}\left[\ln\left(\frac{T_2}{T_1}\right) + \frac{T_1}{T_2} - 1\right]$$

Therefore, during diabatic processes (i.e. heating or cooling), the entropy of the universe increases, as expected from the second law of thermodynamics.

This same procedure can be applied to calorimetric processes. Suppose that a substance of mass m_1, specific heat c_1, and initial temperature T_1 is placed in thermal contact with a second

substance of mass m_2, specific heat c_2, and initial temperature T_2. The final equilibrium temperature of the system is given by the condition that the total internal energy doesn't change and is identical to Equation (4.9). The entropy change is given by

$$dS_{TOTAL} = \frac{\delta Q_{cold}}{T} + \frac{\delta Q_{hot}}{T} = m_1 c_1 \frac{dT}{T} + m_2 c_2 \frac{dT}{T} \Rightarrow \Delta S = m_1 c_1 \ln\left(\frac{T_f}{T_1}\right) + m_2 c_2 \ln\left(\frac{T_f}{T_2}\right)$$

where T_f is the final equilibrium temperature.

4.7 Summary of the Laws of Thermodynamics

The essence of thermodynamics can be summarized by two laws: (1) energy is conserved and (2) entropy increases. These statements are deceptively simple, but they contain an exceptional amount of insight into the nature and behavior of the macroscopic systems. The mathematical content of the 1st and 2nd law can be summarized by Gibbs equation. For an infinitesimal quasistatic change in internal energy, the 1st law can be written as

$$dU = T\, dS - P\, dV + \mu\, dN$$

In this expression, we have four basic state variables (P, T, V, N) and three basic state functions (U, S, μ). With these state functions and state variables, we have six thermodynamic response functions, which describe how a given thermodynamic system responds to energy transfer via heat and/or work

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \quad B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

$$C_V = \left(\frac{\delta Q}{dT}\right)_V, \quad C_P = \left(\frac{\delta Q}{dT}\right)_P$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

A question that can be raised is: how are the response functions connected to laws of thermodynamics? In the next chapter, we will demonstrate that *all* of the consequences of the laws of thermodynamics are mathematically contained in the geometry of a single fundamental system in thermodynamic phase space, defined as $U = U(S, V, N)$. This leads us to discuss the mathematical foundation of classical thermodynamics.

Chapter 5: The Fundamental Surface

We concluded Chap. 4 with a combination of the two foundational laws of thermodynamics to produce a single differential equation known as the Gibbs equation. In principle the Gibbs equation may be integrated to obtain a fundamental surface $U = U(S, V)$ for a substance. The natural, or characteristic dependence of the internal energy U on the variables S and V appearing here is a result of the physics of the work/energy relationship of the first law and the heat/entropy relationship of the second law. We have then a single geometrical surface that contains all the information we require, or can possess, about the substance we are studying and thermodynamics becomes the study of the geometry of this surface. We must only make this study practical in terms of what can be discovered in the laboratory and what is required in application. In this we identify two problems.

1. The function $U = U$ (S, V) is an abstract relationship. We can measure neither energy nor entropy directly in the laboratory. Energy and entropy must be calculated in terms of laboratory variables, which are temperature, pressure, and volume or density. We must then find ways to relate the properties of this fundamental surface to laboratory variables.

2. Although the fundamental surface must exist for each substance, we can only obtain this as a function in closed form for the simplest of substances. Our practical work will involve small variations in one property or another. In essentially all cases we must make approximations and we must deal with tabulated data.

To deal with these problems we must have a basic understanding of the structure of general surfaces. This is a mathematical problem and we begin with a basic mathematics required to address this question.

5.1 Mathematical Review

5.1.1 Geometric View of Partial Derivatives

We begin by considering the variable z as an arbitrary function of x and y, that is $z = z(x, y)$. This is a surface in (x, y, z) – space such as that illustrated in Figure 5.1. Let us consider a differential vector displacement $d\vec{C}$ between the points (0) and (1) on the surface $z = z(x, y)$, which is illustrated in Figure 5.2. The vector $d\vec{C}$ must remain on the surface $z = z(x, y)$.

Therefore, there must be a relationship among the displacements dx, dy, and dz. Because $(dx)_y$ and $(dy)_x$ are infinitesimals, we may write the general change in z resulting from changes in both x and y as a linear sum of two separate changes.

$$dz = (dz)_x + (dz)_y = \frac{(dz)_y}{(dx)_y}(dx)_y + \frac{(dz)_y}{(dy)_x}(dy)_x = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dx \quad (5.1)$$

The partial derivatives are the slope of the tangent lines to the surface shown in Figure 5.3. The slopes of these lines depend on the point on the surface at which they are evaluated.
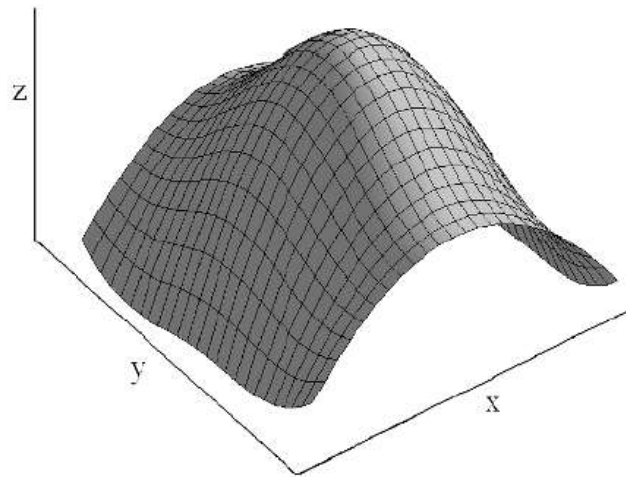
Figure 5.1 A surface $z = z(x, y)$. The coordinate z is the vertical distance above the (x, y) plane. The surface is defined by the values of z specified by $z = z(x, y)$
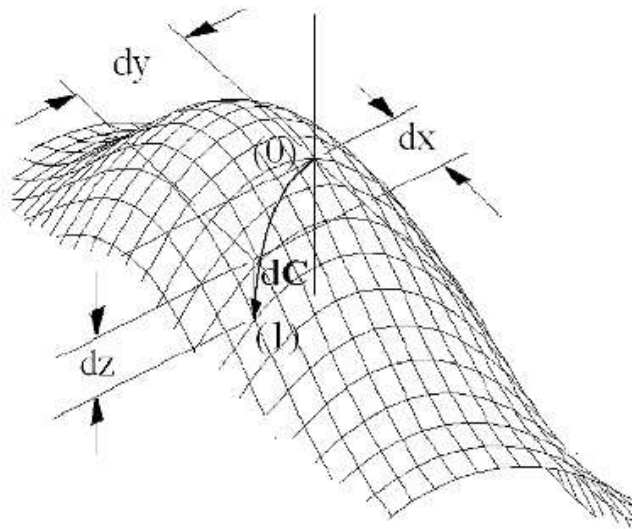
Figure 5.2 Graphical illustration of a differential vector $d\vec{C}$ from (0) to (1) on the surface $z = z(x, y)$

104
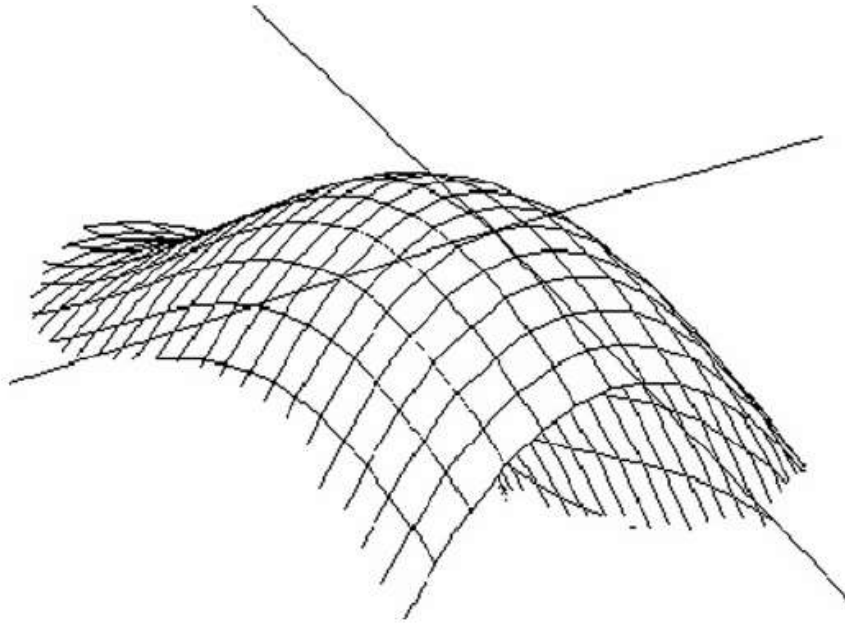
Figure 5.3 Tangent lines. The *two lines* shown lie in planes perpendicular to the x- and y-axes. These lines define a plane tangent to the surface $z = z(x, y)$

The linear sum in Equation (5.1) is called **Pfaff's differential form**, or a **Pfaffian**. The Pfaffian is a linear differential form relating arbitrary differential changes in dx and dy to the resultant differential change dz with the requirement that each point (x, y, z) lies on the surface $z = z(x, y)$. The Pfaffian in Equation (5.1) is an exact differential – that is Equation (5.1) is the differential of a specific function $z = z(x, y)$.
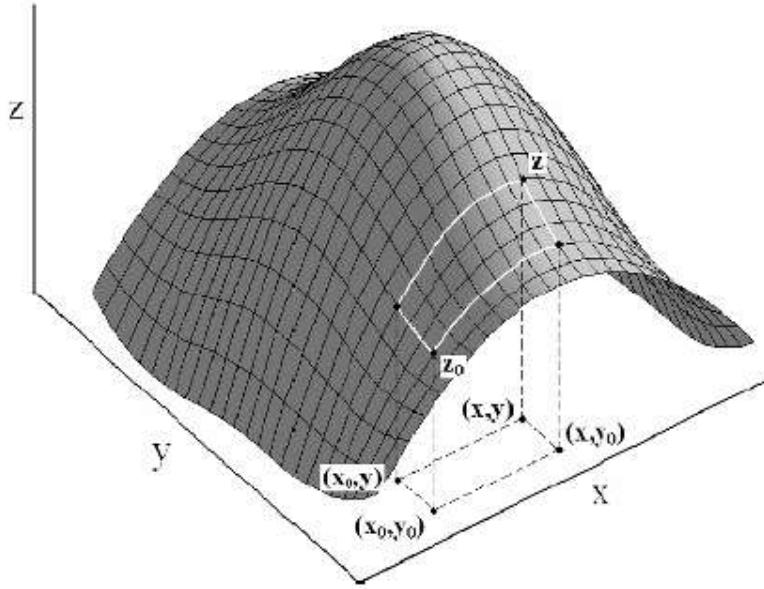
Figure 5.4 Surface $z = z(x, y)$ with contours for integration. To determine the value of z at any arbitrary point on the surface, we must move along the surface. This is the concept of contour integration.

A linear differential form that is an exact differential can, in principle, be integrated to obtain the original function. Let's assume that we only have the Pfaffian for z given in Equation (5.1) and we require the function (surface) $z = z(x, y)$. To find $z = z(x, y)$, we must integrate the Pfaffian and this must be done along a contour. Let us assume that we know, or specify the value of the function $z = z(x, y)$ at some point (x_0, y_0). This point is indicated in the horizontal (x, y) plane below the surface $z = z(x, y)$ in Figure 5.4. The value of z at this point, which we shall call z_0, is indicated as the point at which the vertical line from (x_0, y_0) intersects the surface. If we knew the form of the surface $z = z(x, y)$, we could move our point on the surface from z_0 following either of the white contours shown in Figure 5.4. That is actually what is done in contour integration. We do not know the surface, but we do know the tangents to the surface as shown in Figure 5.3. We can use these tangents to make certain we stay on the surface as we move from z_0 to z. If we choose to move along the white contour from (x_0, y_0) to the point (x, y_0), we hold y constant at the value y_0 and move a distance $dz = (\partial z / \partial x)_y$ for each dx. At the end of the contour, we have then increased in elevation in z from z_0 to

$$z_0 + \int_{x=x_0}^{x} \left(\frac{\partial z}{\partial x}\right)_y dx$$

Now we do the same thing following the second leg of the contour form the intermediate point above (x, y_0) to the final point above (x, y). We now hold x constant at its final value and increase our value of z in accordance with $dz = (\partial z / \partial x)_y$ as we move each distance dy. When get to the final point above (x, y), we have then a final value of z given by

106

$$z = z_0 + \int\limits_{x=x_0}^{x} \left(\frac{\partial z}{\partial x}\right)_y dx + \int\limits_{y=y_0}^{y} \left(\frac{\partial z}{\partial y}\right)_x dy$$

When we recall that

$$\int\limits_{z_0}^{z} dz = z(x,y) - z_0$$

we realize that what we have is the mathematical definition of a contour integral:

$$\int\limits_{z_0}^{z} dz = \int\limits_{x=x_0}^{x} \left(\frac{\partial z}{\partial x}\right)_y dx + \int\limits_{y=y_0}^{y} \left(\frac{\partial z}{\partial y}\right)_x dy$$

Our choice of contours is arbitrary as long as we have a Pfaffian, i.e. an exact differential. For example, we could have in the y-direction first and taken the second contour. It is usually helpful, however, to draw the contours in the plane of the independent variables as a reminder of the variable to be held constant along each contour.

We may obtain partial derivatives of a function to any order. Second partial derivatives are of particular interest to us because the order of partial differentiation makes no difference – that is, for the function $z = z(x,y)$ we have

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

A proof of this property of partial derivatives may be found in any text on multi-variable calculus. This is particular useful in thermodynamics for relating state variables to state functions. For example, if we write Gibbs equation as $dU = T\,dS - P\,dV$, we see that

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Since

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

5.1.2 Differential Relationships

Much of our reasoning in thermodynamics is done with differential equations. In this section, we shall derive certain relationships among partial derivative that will be indispensable in dealing with differentials.

Reciprocals: The Pfaffian for the function $f = f(x, y)$ is

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

If we hold one of the independent variables constant, for example, the variable x, then the above expression becomes

$$(df)_x = \left(\frac{\partial f}{\partial y}\right)_x (dy)_x$$

Using the definition of partial derivative, the above expression becomes

$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial f}\right)_x} \qquad (5.2)$$

This is a general relationship for the partial derivatives of functions of two independent variables. It can be extended to functions of an arbitrary number of variables. For a function of the variables (x, y, z) for example

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = \frac{1}{\left(\frac{\partial y}{\partial f}\right)_{x,z}}$$

Cyclic Permutation: For a constant f, the Pfaffian for the function f has the following form

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0$$

Using the definition of the partial derivative, this expression becomes

$$-\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_f$$

Using the reciprocal relationship of Equation (5.2), we have

$$\left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial x}{\partial f}\right)_y \left(\frac{\partial y}{\partial x}\right)_f = -1 \quad (5.3)$$

This is the **cyclic permutation relationship** among derivatives for functions of two independent variables.

5.1.3 Legendre Transformation

In actual practice, the fundamental surface $U = U(S, V)$ is not particularly convenient because the entropy is not a directly measurable property. Representations of thermodynamic properties in terms of (T, V) or (T, P) are more suitable. It is possible to transform $U = U(S, V)$ into equivalent fundamental surfaces, which have characteristic dependencies on other sets of variables. As fundamental surfaces, these will each contain the same information as $U = U(S, V)$. This is accomplished by the **Legendre transformation**. Because of the central importance of the Legendre transformation to thermodynamics, we shall discuss the formulation in some detail.
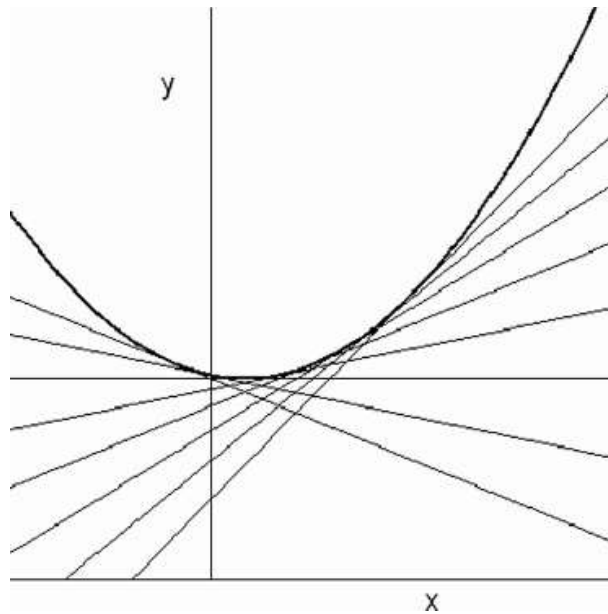
Figure 5.5 Point and tangent line representation of a curve. The original curve can be represented completely by tangent lines.

A single-valued curve in two dimensions, $y = y(x)$, represents a point relationship between the coordinates x and y. To each point x, there corresponds a definite point y. This curve may also be constructed as an envelop of straight lines each of which is tangent to the curve.

This is illustrated, geometrically for a limited number of such tangent lines, in Figure 5.5. Each straight tangent line can be defined by its slope α and intercept β (with the y-axis). There is then a continuous functional relationship $\beta = \beta(\alpha)$ defined by the continuum of points along the curve in Figure 5.5. The function $\beta = \beta(\alpha)$ is a different, but completely equivalent representation of the relationship $y = y(x)$.

We now make this more definite. We begin with the general equation for the tangent lines, which is $y = \alpha x + \beta$. The slope and intercept are functions of the point through which the tangent line passes, which is $\big(x, y(x)\big)$ on the original point curve. So we may write the tangent line equation as

$$\beta = y(x) - \alpha(x)x$$

The differential of this expression gives

$$d\beta = \frac{dy}{dx}dx - \frac{dy}{dx} - xd\alpha = -xd\alpha \Rightarrow \frac{d\beta}{d\alpha} = x(\alpha)$$

which assumes that $\alpha(x) = dy/dx$ may be inverted to obtain $x = x(\alpha)$. That is β is actually a function only of α, which is the transformation we sought. The transform (known as the Legendre transformation) is given by

$$\beta = y\big(x(\alpha)\big) - \alpha x(\alpha)$$

As an example of the Legendre transformation, we consider the function $y(x) = 3x^2 - x + 5$, which is the function that is plotted in Figure 5.5. Taking the derivative of $y(x)$ gives

$$\frac{dy}{dx} = \alpha(x) = 6x - 1 \Rightarrow x(\alpha) = \frac{\alpha + 1}{6}$$

Therefore, the Legendre transformation becomes

$$\beta = y\big(x(\alpha)\big) - \alpha x(\alpha) = 3\left(\frac{\alpha + 1}{6}\right)^2 - \left(\frac{\alpha + 1}{6}\right) + 5 - \left(\frac{\alpha + 1}{6}\right)\left[6\left(\frac{\alpha + 1}{6}\right) - 1\right]$$
$$= -\frac{1}{12}(\alpha + 1)^2 + 5$$
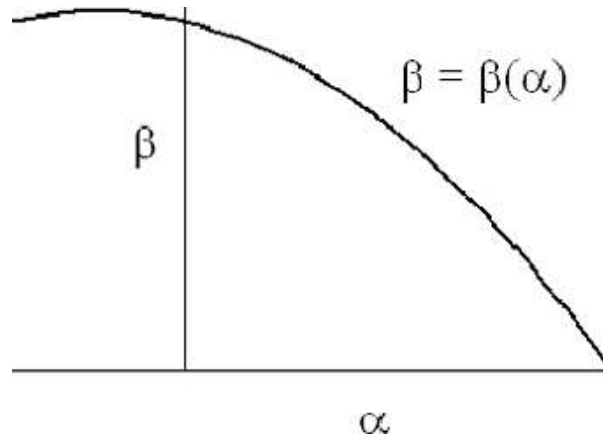
Figure 5.6 Plot of $\beta = \beta(\alpha)$ which corresponds to Figure 5.5

$\beta = \beta(\alpha)$ has been plotted in Figure 5.6. The form of the function $\beta = \beta(\alpha)$ in Figure 5.6 differs from the form of $y = y(x)$ plotted in Figure 5.5
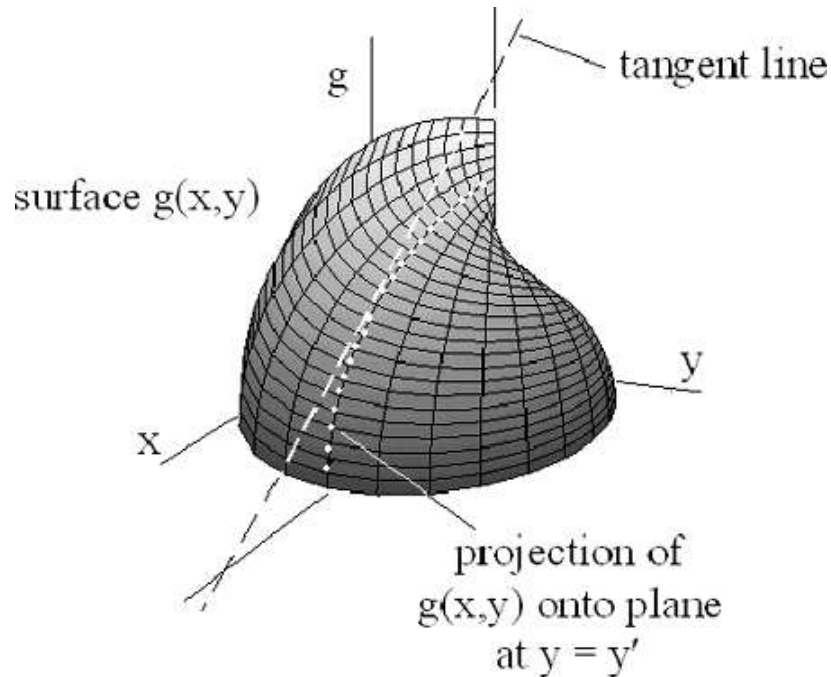
Figure 5.7 Slope/intercept representation of a contour on a surface. This contour is similar to the curve in Figure 5.5. It can be represented by tangent lines

     For functions of two independent variables, the Legendre transformation is similar to that for one. We consider for example, the arbitrary surface $g = g(x, y)$ in Figure 5.7. In Figure 5.7, the dotted curve on the surface $g = g(x, y)$ is the intersection of the surface with the plane perpendicular to the y-axis and passing through a point $y = y'$. This curve, $g(x, y')$, with y' fixed, can be represented by an infinite family of tangent lines as before. The slopes of these

111

lines $\alpha(x, y')$ are the partial derivatives $(\partial g/\partial x)_y$ evaluated at $y = y'$. At each value of y, the Legendre transformation is

$$\beta = g(x, y) - \alpha(x, y)x$$

The differential of β is

$$d\beta = \left(\frac{\partial g}{\partial y}\right)_x dy - x d\alpha$$

Therefore, in this instance of two independent variables, β is a function of y and α. The Legendre transformation has then resulted in a function $\beta(\alpha, y)$. Just as in the case of the single independent variable, we must now insert $x = x(\alpha, y)$, obtained from $\alpha(x, y) = (\partial g/\partial x)_y$, into the final expression for β.

(a)   (b)
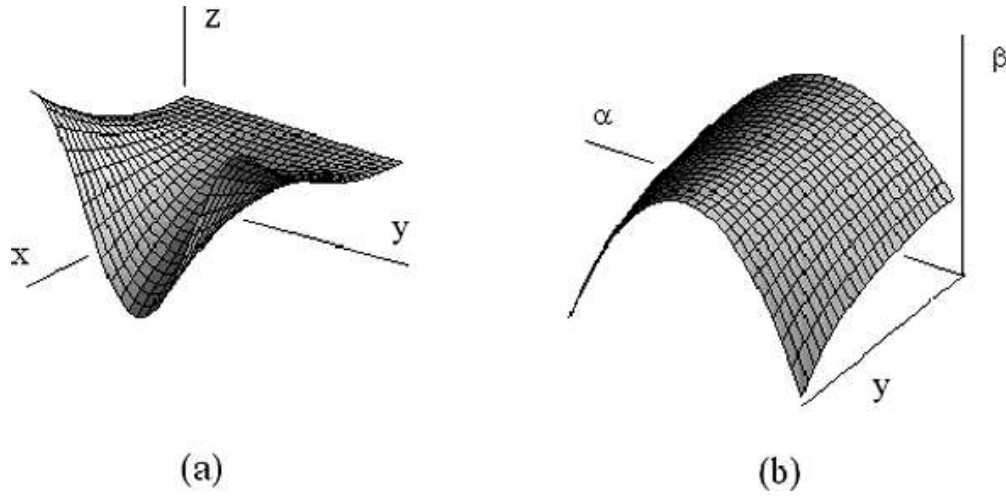
Figure 5.8 The function $z(x, y) = x^2 \cos(y)$ (a) and its Legendre transform (b)

As an example of the Legendre transform of a function of two independent variables, we transform the function $z(x, y) = x^2 \cos(y)$, removing the dependence on x and replacing that with a dependence on $(\partial z/\partial x)_y$, which we shall continue to designate as α. For this example,

$$\alpha(x, y) = \left(\frac{\partial z}{\partial x}\right)_y = 2x \cos(y) \Rightarrow x(\alpha, y) = \frac{\alpha}{2 \cos(y)}$$

Therefore, it can be shown that our Legendre transform is

$$\beta = z(x, y) - \alpha(x, y)x = -\frac{\alpha^2}{4 \cos(y)}$$

We have plotted the original function and the transformed function of the preceding example in Figure 5.8 (a) and (b). These plots illustrate the fact that the form of the transformed surface is in

general very different from that of the original surface. Nevertheless the surfaces are completely equivalent.

We may generalize the Legendre transformation to any number of variables, since the transformation only deals with a single variable and the partial derivative of the original function with respect to that variable. For example, we may replace the dependence of a general function $\Phi(x_1, x_2, \ldots, x_N)$, on the variable x_j in favor of a dependence on the partial derivative $(\partial\Phi/\partial x_j)$. The transformation produces a completely equivalent function $\Psi(x_1, \ldots, x_{j-1}, (\partial\Phi/\partial x_j), x_{j+1}, \ldots, x_N)$ defined by

$$\Psi = \Phi - \left(\frac{\partial\Phi}{\partial x_j}\right)x_j \quad (5.4)$$

5.1.4 General Curvature Relationships

There are general relationships among the curvatures of surfaces related by Legendre transformations. To establish these, we consider a function $f(x, y)$, which we wish to transform into a function $g(x, z)$ by replacing the variable y with $z = (\partial f/\partial y)_x$. The Legendre transform for this function is given by

$$g(x, z) = f[x, y(x, z)] - y(x, z)z$$

If we take the partial derivative of both sides with respect to the untransformed variable, we have

$$\left(\frac{\partial g}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y$$

Taking the second partial derivative of both sides with respect to the untransformed variable results in

$$\left(\frac{\partial^2 g}{\partial x^2}\right)_z = \left(\frac{\partial^2 f}{\partial x^2}\right)_y + \left(\frac{\partial^2 f}{\partial y\partial x}\right)\left(\frac{\partial y}{\partial x}\right)_z \quad (5.5)$$

Taking the second partial derivative of the Legendre transform with respect to the transformed variable gives us

$$\left(\frac{\partial^2 g}{\partial z^2}\right)_x = -\left(\frac{\partial y}{\partial z}\right)_x = -\frac{1}{\left(\frac{\partial^2 f}{\partial y^2}\right)_x} \quad (5.6)$$

Equations (5.5) and (5.6) relate the curvatures of the surfaces connected by a Legendre transformation

5.2 The Fundamental Surface

We shall limit our initial treatment to homogeneous systems containing pure substances. Inhomogeneities can only exist under conditions of nonequilibrium, and equilibrium is required to define thermodynamic variables such as temperature and pressure. We begin our formulation of the fundamental surface with the Gibbs equation, which we repeat here in the form

$$dU = TdS - PdV \quad (5.7)$$

As we noted in Chapter 4, the Gibbs equation is an exact differential relationship among dU, dS and dV of a universal character. The surface $U = U(S,V)$, which can be obtained from (5.7) through contour integration, is then a universal characteristic relationship among U, S and V. The relationships $T = T(S,V)$ and $P = P(S,V)$ required in the integration are unique to each substance. So the surface $U = U(S,V)$ is unique to each substance. This is the fundamental surface for the substance.

Since Equation (5.7) is an exact differential, it is a Pfaffian – that is

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Comparing the above expression to Gibbs equation, we can identify the thermodynamic temperature and thermodynamic pressure as partial derivatives of the fundamental surface with respect to its characteristic variables. Specifically, we have

$$T(S,V) = \left(\frac{\partial U}{\partial S}\right)_V, \quad P(S,V) = -\left(\frac{\partial U}{\partial V}\right)_S \quad (5.8)$$

Equation (5.8) is considered definitions of the thermodynamic temperature and thermodynamic pressure and is universally valid for any and all substances under conditions of thermodynamic equilibrium regardless of the form of the equation of state for the substance. We cannot overemphasize the importance of this identification. Max Planck considered (5.8) a crucial foundation of his investigations of the blackbody radiation spectrum that led to the first identification of the quantum of action in 1900 and this relationship is again central in Einstein's

paper proposing the photon as a quantum of the electromagnetic wave. Neither Planck nor Einstein would relinquish the foundational importance of this definition.

5.2.1 The Fundamental Surface for an Ideal Gas

The ideal gas has the equation of state (per mole) $PV = nRT$ and constant specific heats. We can write Gibbs equation in terms of entropy as

$$dS = \frac{dU}{T} + \frac{P}{T}dV = C_V \frac{dT}{T} + nR \frac{dV}{V}$$

Performing a contour integral, we see that the entropy can be written as a function of temperature and pressure as

$$S - S_0 = C_V \ln\left(\frac{T}{T_0}\right) + nR \ln\left(\frac{V}{V_0}\right)$$

Choosing $S_0(T_0, V_0) = 0$ and using non-dimensionalized $T = T/T_0$, $V = V/V_0$, and $S = S/nR$, we have

$$\exp(S) = T^{\frac{1}{\gamma-1}}V$$

From Equation (5.8), the temperature $T(S,V)$ and the pressure $P(S,V)$ is given by

$$T(S,V) = \left(\frac{\partial U}{\partial S}\right)_V = \exp[(\gamma - 1)S]V^{1-\gamma}$$

$$P(s,v) = -\left(\frac{\partial U}{\partial V}\right)_S = \exp[(\gamma - 1)S]V^{-\gamma}$$

Gibbs equation then becomes

$$dU = \exp[(\gamma - 1)S]\,V^{1-\gamma}dS - \exp[(\gamma - 1)S]\,V^{-\gamma}dV$$

Integrating this along a contour from an initial point (S_1, V_1) to a final point (S, V), we have

$$U(S,V) - U_1 = V_1^{1-\gamma}\int_{S_1, V=V_1}^{S} \exp[(\gamma - 1)S]\,dS - \exp[(\gamma - 1)S]\int_{V_1, S}^{V} V^{-\gamma}\,dV$$

$$= \frac{1}{\gamma - 1}\exp[(\gamma - 1)S]\,V^{1-\gamma} - \frac{1}{\gamma - 1}V_1^{1-\gamma}\exp[(\gamma - 1)S_1]$$

The second term on the right hand side depends only on the reference point (S_1, V_1) and may be identified as the term $-U_1$ on the left. This gives us the fundamental surface for the ideal gas in non-dimensional form

$$U(S,V) = \frac{1}{\gamma - 1} \exp[(\gamma - 1)S] \, V^{1-\gamma}$$

From this, we may obtain the thermodynamic temperature and pressure as function of (S, V). The results are those we originally used for the contour integration of the Gibbs equation.
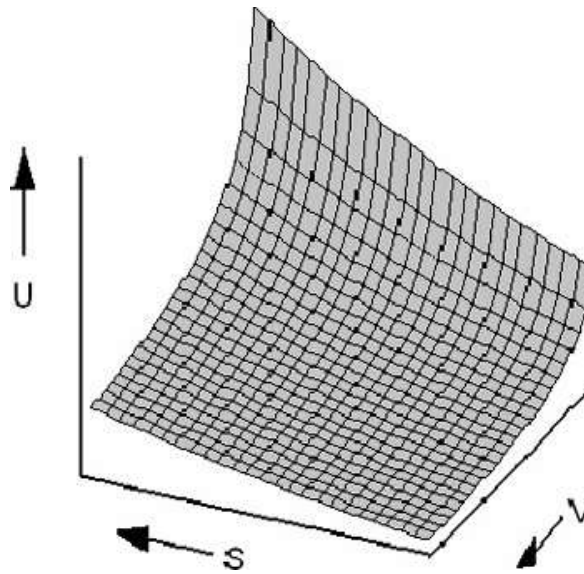
Figure 5.9 The fundamental surface $U=U(S,V)$ for an ideal gas in non-dimensional form

Figure 5.9 gives the plot of the fundamental surface $U = U(S, V)$, which we just found. *All* possible equilibrium states for the substance are points on this fundamental surface. Therefore, any quasistatic reversible process that is physically possible must be representable as a line on this surface. The differential distance between points on the surface is given by the differential form in Equation (5.7). In Figure 5.10(a), an isotherm is drawn on the fundamental surface. All equilibrium thermodynamic states, points on the fundamental surface, lying on this line have the same temperature. In Figure 5.10(b), this isotherm is connected to another isotherm, at a higher temperature, by two lines of constant entropy (adiabats). Thus, Figure 5.10(b) is the Carnot cycle.
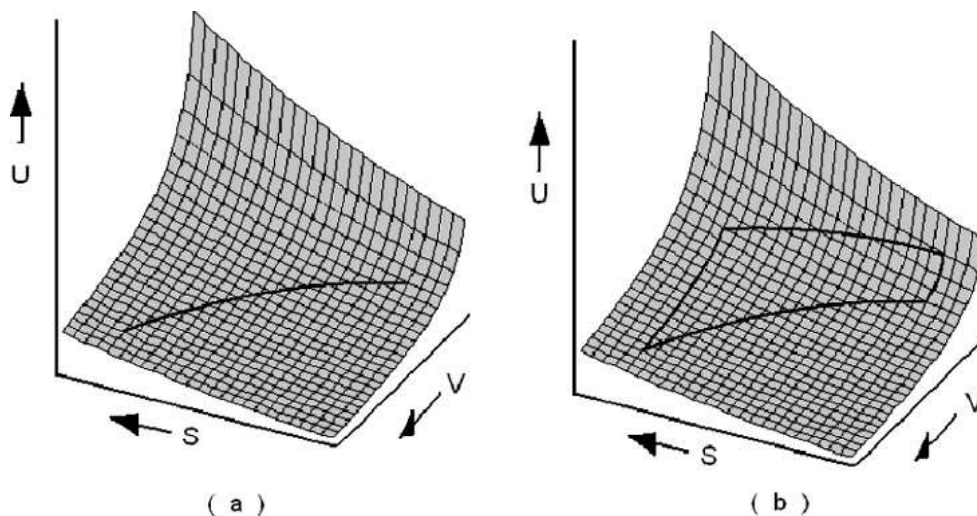
Figure 5.10 The fundamental surface *U=U(S,V)* for an ideal gas with an isotherm (a) and a Carnot cycle (b) depicted on the surface

5.2.2 The Four Thermodynamic Potentials

The representation of the fundamental surface as $U = U(S,V)$ is awkward for many applications because neither the entropy nor the internal energy are laboratory variables. Both of these must be calculated. However, temperature and pressure are laboratory variables and based on the previous section, they can be derived from the fundamental surface. This means that we would like to replace the entropy dependence of the fundamental surface (which is a characteristic variable) with laboratory variables (which are partial derivatives of the fundamental surface with respect to its characteristic variables). Fortunately, we know that the function $U = U(S,V)$ can be transformed into a completely equivalent function using a Legendre transformation as discussed previously.

Using the Legendre transformation we may replace the entropy dependence in $U = U(S,V)$ by a dependence on $T = (\partial U/\partial S)_V$ or the volume dependence on $P = -(\partial U/\partial V)_S$. Because of the properties of the Legendre transformation both of the functions obtained will be completely equivalent to $U = U(S,V)$. The Legendre transformation involves two distinct steps (which we discussed previously):

1. First, obtain the algebraic form of the new function in terms of the original function.
2. Then, algebraically eliminate the transformed variable from the equation obtained in the first step using the partial derivative defining the new variable

117

Let's start by replacing the entropy dependence with a dependence on the thermodynamic temperature (i.e. transform from (S,V) coordinates to (T,V) coordinates). Performing the Legendre transformation gives us a new function:

$$F = U - \left(\frac{\partial U}{\partial S}\right)_V S$$

We must now use the definition $T(S,V) = (\partial U/\partial S)_V$ to solve for $S = S(T,V)$ and eliminate S algebraically from the right hand side of the above expression. After this, we will have

$$F(T,V) = U(T,V) - TS(T,V) \quad (5.9)$$

Equation (5.9) is known as the **Helmholtz free energy** in terms of its characteristic variables (T,V). Because of the equivalence of $U = U(S,V)$ and $F = F(T,V)$, the differential of the Helmholtz free energy $dF = dU - T\,dS - S\,dT$ is equivalent to the Gibbs equation (5.7). Comparing this differential form to Gibbs equation gives us

$$dF = -P\,dV - S\,dT \quad (5.10)$$

which is the Pfaffian of the fundamental surface in the coordinates T and V,

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

Comparing the above expression to Equation (5.7) indicates that

$$P(T,V) = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S(T,V) = -\left(\frac{\partial F}{\partial T}\right)_V$$

We recognize $P = P(T,V)$ as the thermal equation of state for the substance. Therefore, if we have the Helmholtz free energy for a substance in terms of its characteristic variables (T,V), we have the thermal equation of state for that substance. However, we cannot obtain the Helmholtz free energy from the thermal equation of state. To obtain the Helmholtz free energy, we must integrate the Pfaffian of F along a contour in the (T,V) plane, which requires knowledge of the partial derivatives of the Helmholtz free energy. That is we need both the thermal equation of state and $S(T,V)$ for the substance in order to obtain the Helmholtz free energy.

Now, let's replace the volume dependence of $U(S,V)$ with a dependence on the thermodynamic pressure (i.e. transform from (S,V) to (S,P) coordinates). Performing the Legendre transformation gives us a new function:

$$H = U - \left(\frac{\partial U}{\partial V}\right)_S V$$

We must now use the definition $P(S,V) = -(\partial U/\partial V)_S$ to solve for $V = V(S,P)$ and eliminate V algebraically from the right hand side of the above expression. After this, we will have

$$H(S,P) = U(S,P) + PV(S,P) \quad (5.10)$$

Equation (5.10) is known as the **enthalpy** in terms of its characteristic variables (S,P). Because of the equivalence of $U = U(S,V)$ and $H = H(S,P)$, the differential of the enthalpy $dH = dU + P\ dV + V\ dP$ is equivalent to the Gibbs equation (5.7). Comparing this differential form to Gibbs equation gives us

$$dH = T\ dS + V\ dP \quad (5.11)$$

which is the Pfaffian of the fundamental surface in the coordinates S and P,

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Comparing the above expression to Equation (5.7) indicates that

$$T(S,P) = \left(\frac{\partial H}{\partial S}\right)_P, \quad V(S,P) = -\left(\frac{\partial H}{\partial P}\right)_S$$

Finally, let's replace the volume dependence and the entropy dependence of $U(S,V)$ with a dependence on the thermodynamic temperature and the thermodynamic pressure (i.e. transform from (S,V) to (T,P) coordinates). Performing the double Legendre transformation gives us a new function:

$$G = U - \left(\frac{\partial U}{\partial S}\right)_V S - \left(\frac{\partial U}{\partial V}\right)_S V$$

Writing this expression in terms of the new characteristic variables gives

$$G(T,P) = U(T,P) - TS(T,P) + PV(T,P) \quad (5.12)$$

Equation (5.12) is known as the **Gibbs free energy** in terms of its characteristic variables (T,P). Because of the equivalence of $U = U(S,V)$ and $G = G(T,P)$, the differential of the enthalpy

$dG = dU - S\,dT - T\,dS + P\,dV + V\,dP$ is equivalent to the Gibbs equation (5.7). Comparing this differential form to Gibbs equation gives us

$$dG = -S\,dT + V\,dP$$

which is the Pfaffian of the fundamental surface in the coordinates T and P,

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Comparing the above expression to Equation (5.7) indicates that

$$S(T,P) = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V(T,P) = \left(\frac{\partial G}{\partial P}\right)_T$$

In Figure 5.11, we have plotted $U(S,V)$, $F(T,V)$, $H(S,P)$, and $G(T,P)$ for an ideal gas. From a comparison of the forms of the surface, we can see how the geometric form of a simple surface can change in a set of Legendre transformations.
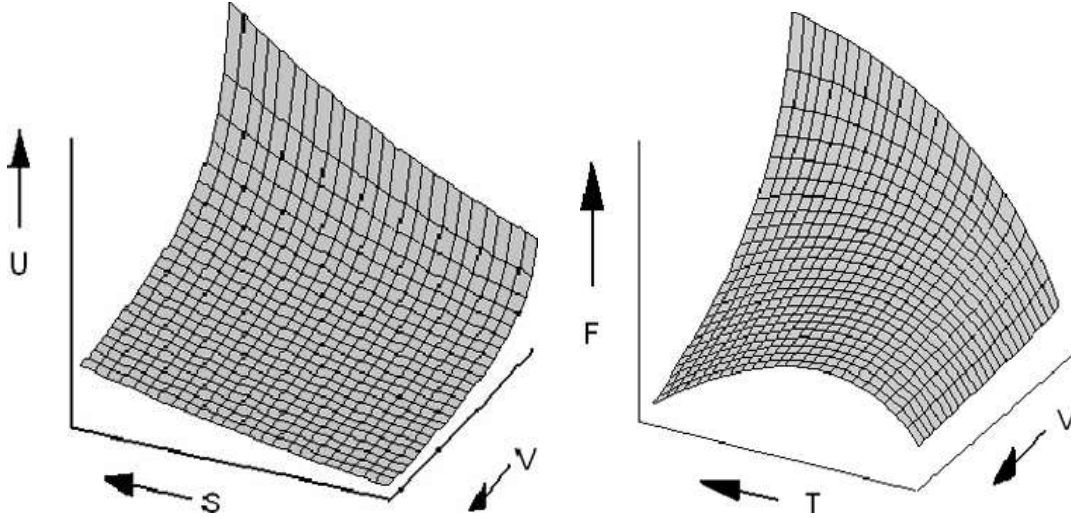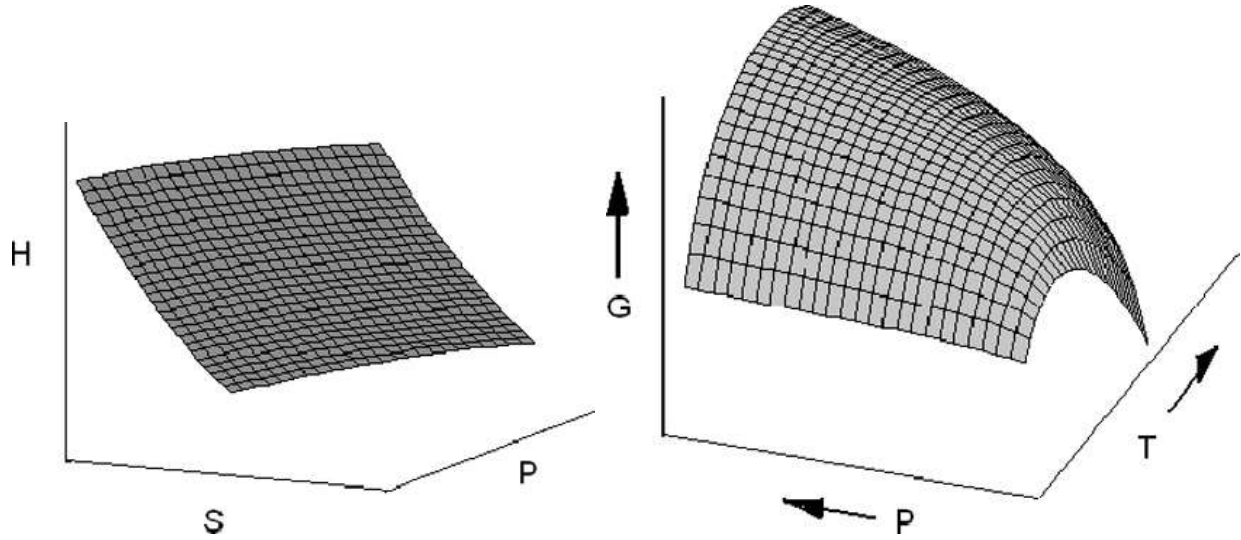
Figure 5.11 Internal energy, Helmholtz free energy, enthalpy, and Gibbs energy for an ideal gas

These four functions are known as **thermodynamic potentials**. The designation of the internal energy U as a thermodynamic potential has its origin in classical mechanics where we speak of the kinetic and potential energies of a moving body. We consider a body moving in the (x, y) plane where there is a conservative force with components $F_x = -(\partial\Phi/\partial x)$ and $F_y = -(\partial\Phi/\partial y)$ from the potential energy $\Phi = \Phi(x, y)$. In classical mechanics, we refer to the forces F_x and F_y as conjugate to the coordinates x and y, respectively. The work done on the body in moving a differential distance with components dx and dy is

$$F_x dx + F_y dy = -\left(\frac{\partial\Phi}{\partial x}\right) dx - \left(\frac{\partial\Phi}{\partial y}\right) dy$$

The right hand side of this equation is the Pfaffian for $-d\Phi$ – that is the work done on the body in the differential distance (dx, dy) is $-d\Phi$. This work increases the kinetic energy of the body at the expense of a loss in potential energy.

In similar way, internal energy $U = U(S, V)$ is the thermodynamic analog of the mechanical potential energy $\Phi = \Phi(x, y)$. In this sense, the partial derivatives of the thermodynamic internal energy are termed **generalized forces** conjugate to the generalized coordinates volume and entropy. This analogy is intuitive for processes taking place at constant entropy. At constant entropy, we have work done on the surroundings at the expense of a loss in internal energy

$$-[dU]_S = -\left(\frac{\partial U}{\partial V}\right)_S dV = P \, dV$$

The thermodynamic pressure, which is a physical force per unit area, is then the (generalized) force conjugate to the (generalized) coordinate V, since the product $P\,dV$ is the work done on the surroundings during an infinitesimal change in the volume.

The reason for using the adjective "generalized" becomes more evident when we consider changes in the entropy

$$-[dU]_V = -\left(\frac{\partial U}{\partial S}\right)_V dS = -T\,dS$$

In keeping with our analogy of dU with $d\Phi$, the thermodynamic temperature is the generalized force conjugate to the generalized coordinate S. At constant volume, changes in entropy (such as the dispersal of heat) come at the expense of internal energy. We have then two pairs of conjugate variables (T, S) and (P, V), appearing in the thermodynamic potential $U = U(S, V)$. Similar ideas hold for the remaining three thermodynamic potentials.

In each of the Legendre transformations of the thermodynamic potentials, we produced products of the conjugate variables (T, S) and (P, V). This is because the conjugate variables (T, S) and (P, V) are linked as $T\,dS$ and $P\,dV$ in the differential of the internal energy and the equivalence of the differential of each potential to the Gibbs equation (5.7) results in a preservation of terms $T\,dS$, $S\,dT$, $P\,dV$, or $V\,dP$ in the forms of the differentials dU, dF, dH, and dG. In particular, each Legendre transformation of a thermodynamic potential replaces one of the conjugate variables in either of the sets (T, S) or (P, V) with the other variable in that set. Since there are only two pairs of conjugate variables, there are only four possible combinations of these variables.

5.2.3 Maxwell Relations

The Legendre transformations produced definitions of the thermodynamic variables T, S, P, and V in terms of the partial derivatives of the thermodynamic potentials. Because the order of partial differential is immaterial, these definitions of thermodynamic variables in terms of partial derivatives of the potentials result in new relationships among the variables. For example, $U = U(S, V)$, we note

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

Since we know that

$$T(S, V) = \left(\frac{\partial U}{\partial S}\right)_V, \quad P(S, V) = -\left(\frac{\partial U}{\partial V}\right)_S$$

then we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$

This is one of what are called the **Maxwell relations** of thermodynamics. Maxwell's relations allow us to substitute a dependence of non-laboratory variables (such as entropy) with a laboratory variable dependence (such as volume). We obtain the remaining Maxwell relations in the same by equating the second mixed partial derivatives of the enthalpy, Helmholtz free energy, and Gibbs free energy. These are

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \qquad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Each of the Maxwell relations expresses a relationship between the two pairs of conjugate variables (T, S) and (P, V) specified by each of the thermodynamic potentials. We identify the potential which is the source for each Maxwell relation from the subscripts of the partial derivatives, which are the characteristic variables for that potential.
Based on the reciprocal relationship derived in Equation (5.2), we can write the Maxwell relations as

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial P}\right)_V}, \quad \left(\frac{\partial T}{\partial V}\right)_P = -\frac{1}{\left(\frac{\partial S}{\partial P}\right)_T}, \quad \left(\frac{\partial T}{\partial P}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial V}\right)_P}, \quad \left(\frac{\partial T}{\partial P}\right)_V = -\frac{1}{\left(\frac{\partial S}{\partial V}\right)_T}$$

When we write the Maxwell relations using the reciprocal relationship, we see that they are sets relations between $(\partial T/\partial V)$ and $(\partial S/\partial P)$ and between $(\partial T/\partial P)$ and $(\partial S/\partial V)$ under various conditions expressed by the subscripts on the partial derivatives. That is the dependencies of (T, S) on (P, V) are such that all four variables appear in each Maxwell relation.

The primary practical use to which we will put the Maxwell relations is to convert some expressions into more understandable forms. We cannot measure the entropy in the laboratory and, therefore, we normally will want to convert partial derivatives involving the entropy into forms involving measurable quantities. The Maxwell relations are often useful in accomplishing this.

5.3 Variable Composition

5.3.1 Intensive and Extensive Variables

The original form of the fundamental surface $U = U(S, V)$ was obtained from a combination of the first and second laws written for a single system containing a specific number of moles of a pure homogeneous substance. Because the substance is pure and homogeneous, the relationships obtained will apply to any large or small amount of the substance. The only limitation is that any subdivision we choose will still have a sufficient number of molecules to be treated as a continuum. We may then define a specific molar internal energy, entropy, or volume as

$$u = \frac{U}{n}, \qquad s = \frac{S}{n}, \qquad v = \frac{V}{n}$$

where n is the number of moles in the original system. Quantities for which the vale depends on the amount of substance present, are termed **extensive variables**.

Each of the three other thermodynamic potentials are mathematically equivalent to $U(S, V)$ and is, therefore, also an extensive variable. We may, then define specific molar enthalpy, Helmholtz free energy, and Gibbs free energy as

$$h = \frac{H}{n}, \qquad f = \frac{F}{n}, \qquad g = \frac{G}{n}$$

Partial differentiation of one of the potentials with respective to an extensive variable results in a variable that is independent of the number of moles present. Thus, we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial u}{\partial s}\right)_v, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial u}{\partial v}\right)_s$$

The thermodynamic temperature and pressure are uniform throughout an equilibrium system and independent of the amount of substance present in the system. Variables which are independent of the amount of the substance in the system are called **intensive variables.**

We note that each of the pairs of conjugate variables (T, S) and (P, V) that link the thermodynamic potentials consists of one extensive and one intensive variable. This is because the produce of the variables in each set must be extensive, as are the potentials. We obtain the intensive variable in each pair by partial differentiation of a thermodynamic potential with respect to the extensive variable of the pair. Correspondingly, we obtain the extensive variable in

each pair by partial differentiation of a thermodynamic potential with respect to the intensive variable of the pair.

We have thus far considered only closed systems. This limitation is too severe for many practical considerations. Most engineering systems are open. And all biological systems are open. So almost all applications of thermodynamics involve open systems. In the following section we shall investigate the dependence of the thermodynamic potentials on a variation in the number of moles present in the system. We shall first consider only single substances and then the effects of mixing of chemically distinct substances.

5.3.2 Single Components

If the number of moles in the system is variable, then the Pfaffian of each potential must include one of the terms

$$\left(\frac{\partial U}{\partial n}\right)_{S,V} dn, \quad \left(\frac{\partial H}{\partial n}\right)_{S,P} dn, \quad \left(\frac{\partial F}{\partial n}\right)_{T,V}, \quad \left(\frac{\partial G}{\partial n}\right)_{T,P} dn$$

The first three of the partial derivatives appearing in the above expression present difficulties because in each of these the characteristic dependence of the potential is on one of the extensive quantities S and V. These are proportional to the number of moles present, but are held constant in the differentiation. The term involving the Gibbs free energy, however, presents no such difficult because the Gibbs energy depends only on intensive properties. For this reason, the Gibbs free energy is the potential on which the formulation for systems of variable composition is based. Once we have the Pfaffian for $G(T, P, n)$, the Pfaffians for the other potentials can be obtained directly by writing them in terms of the Gibbs free energy and obtaining the differential of the result.

For a single component system with a variable number of moles n, the Gibbs free energy is $G(T, P, n) = ng(T, P)$. We define the **chemical potential** for a single substance $\mu = \mu(T, P)$ as

$$\mu(T, P) \equiv \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

Because T and P are intensive variables, we must have that

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = g(T, P) \Rightarrow \mu(T, P) = g(T, P)$$

125

This means that the chemical potential for a single substance (which we introduced earlier in terms of diffusion) is the Gibbs free energy per mole for the substance. The Pfaffian for the specific (molar) Gibbs energy is

$$dg = -sdT + vdP$$

Thus, the Pfaffian for $G(T,P,n)$ as

$$dG(T,P,n) = n\,dg(T,P) + g(T,P)dn = n(-s\,dT + v\,dP) + \mu\,dn = -S\,dT + V\,dP + \mu\,dn$$

Thus,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n}, \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,n}$$

for single composition systems of variable composition.

The Helmholtz free energy can be written in terms of the Gibbs energy

$$dF(T,V,n) = d[G(T,P,n) - PV] = -S\,dT - P\,dV + \mu\,dn$$

By identifying terms in this Pfaffian, we have

$$S = \left(\frac{\partial F}{\partial T}\right)_{V,n}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,n}$$

This implies that

$$\mu(T,V) = \left(\frac{\partial F}{\partial n}\right)_{T,V}$$

Here $\mu(T,V)$, the chemical potential, is still the molar Gibbs free energy, but written as a function of (T,V). It is not the specific (molar) Helmholtz free energy, which is defined as $f(T,V) = F(T,V,n)/n$.

Applying the same method to the enthalpy and the internal energy gives

$$dU = T\,dS - P\,dV + \mu\,dn$$
$$dH = T\,dS + V\,dP + \mu\,dn$$

so that

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = \left(\frac{\partial H}{\partial S}\right)_{P,n}, \quad P = \left(\frac{\partial U}{\partial V}\right)_{S,n}, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,n}$$

Therefore, the chemical potential appears as a function of (S, V) and (S, P):

$$\mu(S, V) = \left(\frac{\partial U}{\partial n}\right)_{S,V}, \quad \mu(S, P) = \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

Again these are not the specific molar potentials u or h

5.4 Geometric Structure of the Fundamental Surface

In the preceding sections we established the four thermodynamic potentials as the basis of thermodynamics. Using the ideal gas as an example we showed that the geometric form of the potentials varies considerably. Specifically the curvatures of the potentials differ one from the other. In this section we shall relate the curvatures to one another and to actual laboratory quantities. Our final goal is to show specifically how the potentials can be obtained directly from laboratory measurements.

5.4.1 Gibbs-Helmholtz Equations

In this section we shall obtain explicit expressions for the curvatures of the Helmholtz and Gibbs energies along the temperature axis. The path will, lead us through the Gibbs-Helmholtz equations and a general thermodynamic relationship for the difference between the specific heats. We could write down the final relationships almost immediately. Taking the path we have chosen will provide a deeper insight into the potentials and introduce the Gibbs-Helmholtz equations in a readily understandable context.

If we perform a series of Legendre transforms, we can obtain U and H from F and G. That is

$$U(T, V) = F(T, V) - T\left[\frac{\partial F(T, V)}{\partial T}\right]_V$$

$$H(T, P) = G(T, P) - T\left[\frac{\partial G(T, P)}{\partial T}\right]_P$$

In the above expression, we have chosen not to introduce the entropy for the partial derivatives. However, in choosing not to introduce the entropy in either expression, we are forcing the internal energy to remain a function of (T, V), which are the characteristic variables of the Helmholtz free energy and the enthalpy to remain a function of (T, P) which are the characteristic variables of the Gibbs energy. These equations may be written as

$$\frac{U(T,V)}{T^2} = -\frac{\partial}{\partial T}\left(\frac{F(T,V)}{T}\right)_V, \qquad \frac{H(T,P)}{T^2} = -\frac{\partial}{\partial T}\left(\frac{G(T,P)}{T}\right)_P \qquad (5.13)$$

The equation set (5.13) is known as the **Gibbs-Helmholtz equations.** The Gibbs-Helmholtz equations are particularly useful because the entropy, which is not measurable, is missing from them. They provide the internal energy and the enthalpy in terms of very practical laboratory coordinates (T, V) and (T, P), respectively. With the Gibbs-Helmholtz equations, we have a more logical basis for the specific choices of the laboratory variables in which to express U and H.

The Pfaffians for $U(T, V)$ and $H(T, P)$ are

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Using these expressions, we can rewrite Equations (5.7) and (5.11)

$$dU = T\,dS - P\,dV \Rightarrow T\,dS = dU + P\,dV = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

$$dH = T\,dS + V\,dP \Rightarrow T\,dS = dH - V\,dP = C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

These are general expressions from which we may obtain the entropy in terms of (T, V) or (T, P) provided we have determined the specific heats and the dependence of U on V and H on P for the substance of interest.

We may obtain general expressions for the dependence of U on V and H on P using the Maxwell relations. Under conditions of constant temperature, the Pfaffians for dU and dH are

$$[dU]_T = T[dS]_T - P\,[dV]_T$$
$$[dH]_T = T[dS]_T + V\,[dP]_T$$

Using the Maxwell relations associated with F and G,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \quad \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad (5.14)$$

The equation set (5.14) is completely general and a profoundly important relationship because it shows that the volume dependence of the internal energy and the pressure dependence of the enthalpy can be determined if the thermal equation of state is known.

With Equation (5.14), we may produce a universal relationship dT, dV, and dP. Recalling our previous expressions on the Pfaffian for $U(T,V)$ and $H(T,P)$

$$T\,dS = dU + P\,dV = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

$$T\,dS = dH - V\,dP = C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Setting this equal to each other gives

$$C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV = C_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Rearranging this expression gives

$$(C_P - C_V)dT = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV - \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Substituting Equation (5.14) gives

$$(C_P - C_V)dT = T\left(\frac{\partial P}{\partial T}\right)_V dV + T\left(\frac{\partial V}{\partial T}\right)_P dP$$

If P is held constant, then the above example gives us

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Using the cyclic permutation relation (5.3),

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

then

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \qquad (5.15)$$

For any real substance an isothermal increase in pressure results in a decrease in volume – that is $(\partial P/\partial V) < 0$. Therefore, for any real substance, $C_P > C_V$ and the difference can be obtained from the thermal equation of state. Or, even if the thermal equation of state is unknown, the partial derivatives in Equation (5.15) are quantities readily measured in the laboratory. The difference in specific heats can then always be found and it is only necessary to measure one of the specific heats in the laboratory.

5.4.2 Curvatures of the Fundamental Surface

The specific heats may be obtained directly from the Helmholtz and Gibbs free energies. Recall that

$$U(T,V) = F(T,V) - T\left[\frac{\partial F(T,V)}{\partial T}\right]_V \Rightarrow \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial F}{\partial T}\right)_V - \frac{\partial}{\partial T}\left(T\left[\frac{\partial F(T,V)}{\partial T}\right]_V\right)$$

$$\Rightarrow C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V \qquad (5.16)$$

$$H(T,P) = G(T,P) - T\left[\frac{\partial G(T,P)}{\partial T}\right]_P \Rightarrow \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial G}{\partial T}\right)_P - \frac{\partial}{\partial T}\left(T\left[\frac{\partial G(T,P)}{\partial T}\right]_P\right)$$

$$\Rightarrow C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P \qquad (5.17)$$

Even though the specific heats are laboratory quantities, Equation (5.16) and (5.17) show that they are defined thermodynamically in terms of the structure (curvatures) of the fundamental surface.

Finally we observe that if the Helmholtz and Gibbs energies are known as functions of their characteristic variables, then the internal energy and enthalpy are known as functions of

130

laboratory coordinates. But the Helmholtz and Gibbs energies cannot be obtained from integration of the Gibbs-Helmholtz equations because these equations contain only single partial derivatives of the Helmholtz and Gibbs energies. the partial integration of the Gibbs-Helmholtz equations can only provide $F(T,V)$ to within an arbitrary function of the volume and $G(T,P)$ to within an arbitrary function of the pressure.

Because there is no known substance for which the input of heat results in a decrease in temperature, $C_V > 0$ and $C_P > 0$. Therefore, from (5.16) and (5.17), we find that

$$\left(\frac{\partial^2 F(T,V)}{\partial T^2}\right)_V < 0, \quad \left(\frac{\partial^2 G(T,V)}{\partial T^2}\right)_P < 0$$

The curvatures along the temperature axes of both the Helmholtz and Gibbs free energies are then negative for any real substance. This is illustrated in Figure 5.11 for the ideal gas. As mentioned previously, the specific heats are a measure of the response of a substance to heat transfer. They are, therefore, referred to as **caloric quantities**. Since we require knowledge of only one specific heat (see Equation (5.15)) and $C_V(T,V)$ can be found from $U(T,V)$, traditionally the function $U = U(T,V)$ is referred to as the **caloric equation of state**.

We can also show that mechanical response functions may be obtained directly from the Helmholtz and Gibbs free energies. Recall that the coefficient of volume expansion β was defined as

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Using the Pfaffian for G, it can be shown that

$$\beta = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

So the coefficient of volume expansion is known if the Gibbs energy is known as a function of its characteristic variables. Similarly, it can be shown that the isothermal compressibility can be written as

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

The curvature of the Gibbs free energy along the P axis is then determined by the mechanical property κ_T and is negative. This may be seen for the ideal gas in Figure 5.11.

Recall that Helmholtz free energy and the enthalpy may each be obtained directly from the Gibbs free energy

$$H(T,P) = G(T,P) - T\left[\frac{\partial G(T,P)}{\partial T}\right]_P$$

$$F(T,V) = G(T,P,n) - PV$$

From the general curvature relationship in Equations (5.5) and (5.6), we may then find the curvature of the Helmholtz free energy and the enthalpy from the curvature of the Gibbs energy. For example, for the Helmholtz free energy, we have

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = \left(\frac{\partial^2 G}{\partial T^2}\right)_P + \left(\frac{\partial^2 G}{\partial P \partial T}\right)\left(\frac{\partial P}{\partial T}\right)_V = -\frac{C_P}{T} + \beta V\left(\frac{\partial P}{\partial T}\right)_V$$

Using the cyclic permutation relation (5.3), it can be shown that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa_T}$$

Therefore, we have

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = \left(\frac{\partial^2 G}{\partial T^2}\right)_P + \left(\frac{\partial^2 G}{\partial P \partial T}\right)\left(\frac{\partial P}{\partial T}\right)_V = -\frac{C_P}{T} + \frac{\beta^2 V}{\kappa_T}$$

Using the definition of β and κ_T in Equation (5.15) gives

$$C_P - C_V = T\frac{\beta^2 V}{\kappa_T}$$

Using this expression, we obtain

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\frac{C_V}{T}$$

Moreover, from the cyclic permutation relation (5.3), we have

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = \frac{1}{\left(\frac{\partial^2 G}{\partial P^2}\right)_T} = \frac{1}{V\kappa_T}$$

We may continue in this fashion to establish the curvatures for all of the potentials. The results are as follows:

132

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \frac{T}{C_V} \qquad \left(\frac{\partial^2 U}{\partial V^2}\right)_S = \frac{1}{V\kappa_S}$$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_P = \frac{T}{C_P} \qquad \left(\frac{\partial^2 H}{\partial P^2}\right)_S = -V\kappa_S$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_P}{T} \qquad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = -V\kappa_T$$

where $\kappa_S = -(1/V)(\partial V/\partial P)_S$ is known as the **isentropic compressibility** as defined earlier.

We see that the curvatures are all determined from quantities readily obtained in the laboratory. The curvatures along the T and S axes are all determined by caloric properties and the curvatures along the V and P axes are determined by the compressibilities. Of these, κ_S is not strictly mechanical, since its measurement specifies no heat transfer. So there is only a separation into caloric and mechanical curvatures in the case of the Helmholtz and Gibbs energies. All of these properties of the potentials are consequences of the fact that they are connected by the Legendre transformation. As such they are mathematical results and the reader should not necessarily attach any deeper significance to them at this point in the discussion. The deeper significance will emerge when we discuss thermodynamic stability and the physical meaning of the thermodynamic potentials in next chapter. At this stage we have only the separate requirements of caloric stability that the specific heats are positive, and the requirements of mechanical stability that the compressibilities are positive. We will later link these as general requirements of real substances.

5.4.3 From Curvatures to Potentials

The curvatures of the potentials are all laboratory measurable quantities, but we cannot obtain function from knowledge of their second derivatives alone. We must perform a contour integration of a Pfaffian – that is, we must have first partial derivatives of the function. The first partial derivatives of the potentials are equal to T, P, V, or S. We know $T(P,V)$, $P(T,V)$, and $V(T,P)$, if we know the thermal equation of state of the substance and then we must calculate the entropy S. In other words, we must have knowledge of the thermal equation of state and of the entropy in order to obtain the potentials.

We may obtain the thermal equation of state from the Pfaffian for V, which is

$$\frac{dV(T,P)}{V(T,P)} = \beta(T,P)dT - \kappa_T(T,P)dP$$

The Pfaffians for $S(T,P)$ and $S(T,V)$ can be obtained from the curvatures of the Gibbs and Helmholtz energies. These are

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = -\left(\frac{\partial^2 G}{\partial T^2}\right)_P dT - \left(\frac{\partial^2 G}{\partial P \partial T}\right) dP$$

$$\Rightarrow dS(T,P) = C_P \frac{dT}{T} - \beta(T,P)V(T,P)\, dP$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = -\left(\frac{\partial^2 F}{\partial T^2}\right)_V dT - \left(\frac{\partial^2 F}{\partial V \partial T}\right) dV =$$

$$\Rightarrow dS(T,V) = C_V \frac{dT}{T} - \frac{\beta(T,V)}{\kappa_T(T,V)} dV$$

where the last equality uses the cyclic permutation relation (5.3). The contour integration of these expressions will then yield the functions $S(T,P)$ and $S(T,V)$.

We have, therefore, obtained the functions $V(T,P)$ and $S(T,P)$ required for the contour integration of the Pfaffian of G and the functions $P(T,V)$ and $S(T,V)$ required for the contour integration of the Pfaffian of F. To carry out this procedure, we have required only the response functions (which are laboratory quantities) C_V, C_P, β, and κ_T. The difficulty in this program is, however, that the reference value for the entropy S_0 contributes a temperature dependence of TS_0 to the final forms of the Gibbs and Helmholtz energies. That is the part of the temperature dependence of the Gibbs and Helmholtz energies is proportional to the reference value of the entropy. The reference value of the entropy is, therefore, not arbitrary in the same sense that the reference value for the energy was arbitrary. We must, however, specify some value for S_0.

The resolution of this difficulty will be with the third law of thermodynamics. A consequence of that law, although not the law itself, will be that the entropy asymptotically approaches a constant value as the thermodynamic temperature approaches absolute zero. At the suggestion of Max Planck, this constant is chosen is to be zero. We mention this resolution for completeness here.

5.4.4 Mechanical and Caloric Consistency

Two types of laboratory quantities we have identified, i.e the caloric (C_P, C_V, κ_S) and the mechanical (β, κ_T) are not separate. They are linked by the laws of thermodynamics. We may also obtain self-consistency relations between mechanical and caloric quantities from the Pfaffians for the entropy. Since partial derivatives commute, we have

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P$$

which results in

$$\frac{1}{T}\frac{\partial C_P(T,P)}{\partial P} = -\frac{\partial}{\partial T}\big(\beta(T,P)V(T,P)\big) \quad (5.18)$$

Furthermore,

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V$$

which results in

$$\frac{1}{T}\frac{\partial C_V(T,V)}{\partial V} = \frac{\partial}{\partial T}\left(\frac{\beta(T,V)}{\kappa_T(T,V)}\right) \quad (5.19)$$

We can partially integrate these expressions to obtain $C_P(T,P)$ and $C_V(T,V)$, provided we have the values of the specific heats as functions of temperature at reference pressure and volume, which we designate here as P^0 and V^0.

$$C_P(T,P) = C_P(T,P^0) - T\int_{P^0}^{P}\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP$$

$$C_V(T,V) = C_V(T,V^0) + T\int_{V^0}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV$$

Because of the universal relationship in Equation (5.15), this means that Equations (5.18) and (5.19) are not independent. There is then only one self-consistency relationship for the mechanical properties of any substance – either Equation (5.18) or (5.19). Since β and κ_T together determine the thermal equation of state, this is fundamentally a relationship between the thermal equation of state and the caloric behavior of any substance that must hold if the substance is real.

In this chapter we have shown that the curvatures of the potentials are proportional to specific heats and compressibilities, which are quantities that can be measured in the laboratory. We have also been able to find general relationships among specific heats and the compressibilities, which must be valid for the properties of any real substance. This indicates an interdependence of material properties related to the transfer of heat (caloric properties) and

those independent of any heat transfer considerations (mechanical properties). This interdependence is reflected in the fact that to determine one of the thermodynamic potentials, such as the Gibbs energy, requires knowledge of the thermal equation of state and of the entropy for the substance. We have ended the chapter by outlining a path that leads, in principle, directly from laboratory measurable quantities to the potentials. And we have obtained equations that must hold if the laboratory quantities are actually self-consistent. In the next chapter, we will examine the physical meaning of these potentials

Chapter 6: The Thermodynamic Potentials

One of the principal objects of theoretical research in physics is to find the point of view from which the subject appears in its greatest simplicity. In the context of classical thermodynamics, a principle goal is to find the point of view from which the mathematical combination of the laws of thermodynamics appears in its simplest form. Gibbs' great contribution to thermodynamics was to show that the consequences of the laws of thermodynamics were contained in the geometry of a single fundamental surface. This fundamental surface of thermodynamics is the representation of the internal energy of a system as a function of the entropy and the volume: $U = U(S, V)$. In the previous chapter, we began our exploration of this discovery and its consequences. We also used a special coordinate transformation, called the **Legendre transformation**, to obtain three additional equivalent surfaces known as thermodynamic potentials which are functions of (S, P), (T, V), and (T, P). In this chapter, we will examine the physical meanings and applications of the thermodynamic potentials. We will see that the usefulness of the thermodynamic potentials lies in the ease with which they may describe particular thermodynamic systems and processes that occur frequently enough to be of general interest as well as in the deeper intuition they will provide for thermodynamics as a whole.

6.1 Enthalpy

Recall from the previous chapter that enthalpy is defined as

$$H(S, P) = U(S, P) + PV(S, P)$$

The Pfaffian of $H(S, P)$ is given by

$$dH = T \, dS + V \, dP$$

Based on the Pfaffian, we have

$$T(S, P) = \left(\frac{\partial H}{\partial S}\right)_P, \quad V(S, P) = \left(\frac{\partial H}{\partial P}\right)_S$$

The Maxwell relation associated with enthalpy is

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

and finally the curvature of $H(S, P)$ is given by

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_P = \frac{T}{C_P} \qquad \left(\frac{\partial^2 H}{\partial P^2}\right)_S = -V\kappa_S$$

The enthalpy of an ideal gas is given by

$$H = U + PV = \left(\frac{f}{2} + 1\right) NkT$$

What is the physical meaning of enthalpy? This can be answered in several ways. First let's suppose that we attempt to create a thermodynamic system and place it within an environment. In order to perform this, we would need to (1) create the internal energy of the thermodynamic system and (2) use additional energy (equal to PV) to push the environment out of the way to make room for the object. Thus, the total energy required to make the system is the enthalpy.

For any isobaric process, the net enthalpy is given by: $\Delta H = \Delta U + P\Delta V$. This states that enthalpy can increase for two reasons: (1) the internal energy of the system increases and (2) the system expands and does work on its surroundings. Furthermore, for a reversible isobaric process, we have

$$\Delta H = (Q + W) + P\Delta V = Q + (-P\Delta V) + W_{other} + P\Delta V = Q + W_{other}$$

Thus, if no other types of work are being done, the change in enthalpy tells you directly how much heat has been added to the system (this is why we use the symbol H for enthalpy). To reiterate,

The change in enthalpy tells you directly how much heat has been added to or removed from a given system (during isobaric processes).

At this point, we can make a comparison between internal energy and enthalpy. Just as $Q = \Delta U$ for isochoric processes, $Q = \Delta H$ for isobaric processes. This implies that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
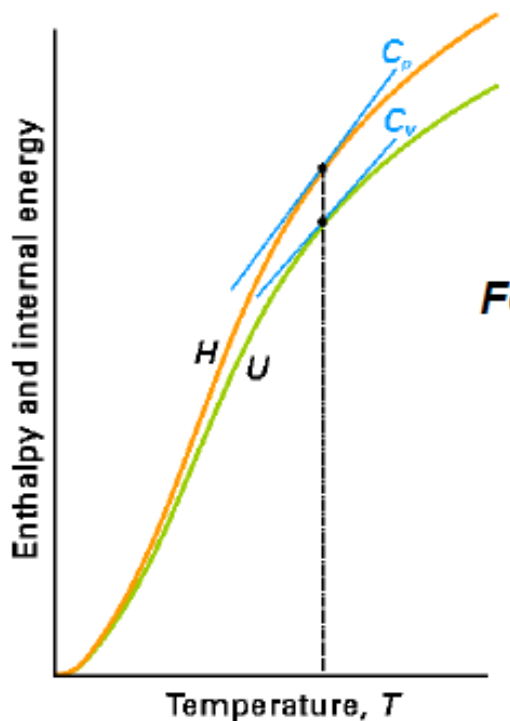
Figure 6.1 Schematic of the temperature dependence of enthalpy and internal energy

Thus, just as C_V should really be called "energy capacity", C_P can be considered "enthalpy capacity".

6.1.1 Chemical Reactions

Since enthalpy includes the work done on the surroundings, it is ideal for understanding heat transfer during chemical reactions. For an **exothermic reaction** at constant pressure, ΔH is the energy *released* in the reaction (including the energy retained in the system and lost through expansion against its environment).

Consider the following general type of reaction:

Reactant →Products
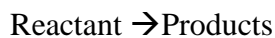
The ΔH is defined as the difference between the enthalpies of products and the reactants. Thus,

$$\Delta H = H_{products} - H_{reactants}$$

The enthalpy of reaction can be positive or negative or zero depending upon whether the heat is gained or lost or no heat is lost or gained. If $\Delta H > 0$, this implies that $H_{products} > H_{reactants}$. In

order for this to happen, energy must be *absorbed* in the reaction from the surroundings (including the energy lost by the system and gained by compression from its environment). Reactions which absorb energy are known as **endothermic reactions**. Conversely, if $\Delta H < 0$, this implies that $H_{products} < H_{reactants}$. In order for this to happen, energy must be *released* from the reaction into the environment (including the energy retained in the system and lost through expansion against its environment). Reactions which release energy are known as **exothermic reactions**. Generally, there are three factors which can affect the enthalpy: (1) the concentrations of the reactants and the products, (2) the temperature of the system, and (3) the partial pressures of the gases involved (if any).

When we write chemical equations to represent chemical reactions, we simply write the balanced chemical equations. However, within the realm of thermodynamics, we must write the chemical equations with the change in heat (i.e. enthalpy change). Such equations are known as **thermochemical equations**. Consider the process of melting the ice, for which we write the following chemical equation:

$$H_2O\ (s) \rightarrow H_2O\ (l)$$
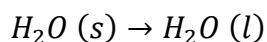
This equation simply says that one mole of ice melts and one mole of water forms. However, in reality, the melting process involves absorption of certain amount of heat by the ice. Now we have to incorporate that heat as a part of the chemical reaction that is indicated by the enthalpy change. When you do this, it becomes a thermochemical equation.

$$H_2O\ (s) \rightarrow H_2O\ (l), \quad \Delta H = 6.01\ kJ/mol$$

The enthalpy change indicates that this is an endothermic reaction – that is, heat is absorbed by the ice from the environment.

A common standard enthalpy change, as shown in the previous example, is the **enthalpy of formation**. Since chemical reactions are reversible, the enthalpy for the reverse process is the negative of the forward change. The table in Figure 6.2 is compiled for 1 mole of material at 298 K and 1 bar. Note that most of the enthalpies of formation are negative, indicating the most reactions are exothermic. Since the flow of heat in any thermodynamic system occurs to maximize entropy of the universe, this implies that chemical reactions occur so as to maximize entropy of the universe or to minimize the enthalpy of the system.

Substance (form)	$\Delta_f H$ (kJ)	Substance (form)	$\Delta_f H$ (kJ)
Al (s)	0	H_2 (g)	0
Al_2SiO_5 (kyanite)	-2594.29	H (g)	217.97
Al_2SiO_5 (andalusite)	-2590.27	H^+ (aq)	0
Al_2SiO_5 (sillimanite)	-2587.76	H_2O (l)	-285.83
		H_2O (g)	-241.82
Ar (g)	0		
		He (g)	0
C (graphite)	0		
C (diamond)	1.895	Hg (l)	0
CH_4 (g)	-74.81		
C_2H_6 (g)	-84.68	N_2 (g)	0
C_3H_8 (g)	-103.85	NH_3 (g)	-46.11
C_2H_5OH (l)	-277.69		
$C_6H_{12}O_6$ (glucose)	-1273	Na^+ (aq)	-240.12
CO (g)	-110.53	NaCl (s)	-411.15
CO_2 (g)	-393.51	$NaAlSi_3O_8$ (albite)	-3935.1
H_2CO_3 (aq)	-699.65	$NaAlSi_2O_6$ (jadeite)	-3030.9
HCO_3^- (aq)	-691.99		
		Ne (g)	0
Ca^{2+} (aq)	-542.83		
$CaCO_3$ (calcite)	-1206.9	O_2 (g)	0
$CaCO_3$ (aragonite)	-1207.1	O_2 (aq)	-11.7
$CaCl_2$ (s)	-795.8	OH^- (aq)	-229.99
Cl_2 (g)	0	Pb (s)	0
Cl^- (aq)	-167.16	PbO_2 (s)	-277.4
		$PbSO_4$ (s)	-920.0
Cu (s)	0		
		SO_4^{2-} (aq)	-909.27
Fe (s)	0	HSO_4^- (aq)	-887.34
		SiO_2 (α quartz)	-910.94
		H_4SiO_4 (aq)	-1449.36

Figure 6.2 Table of the enthalpy of formation for selected substances

6.1.2 The Rankine cycle
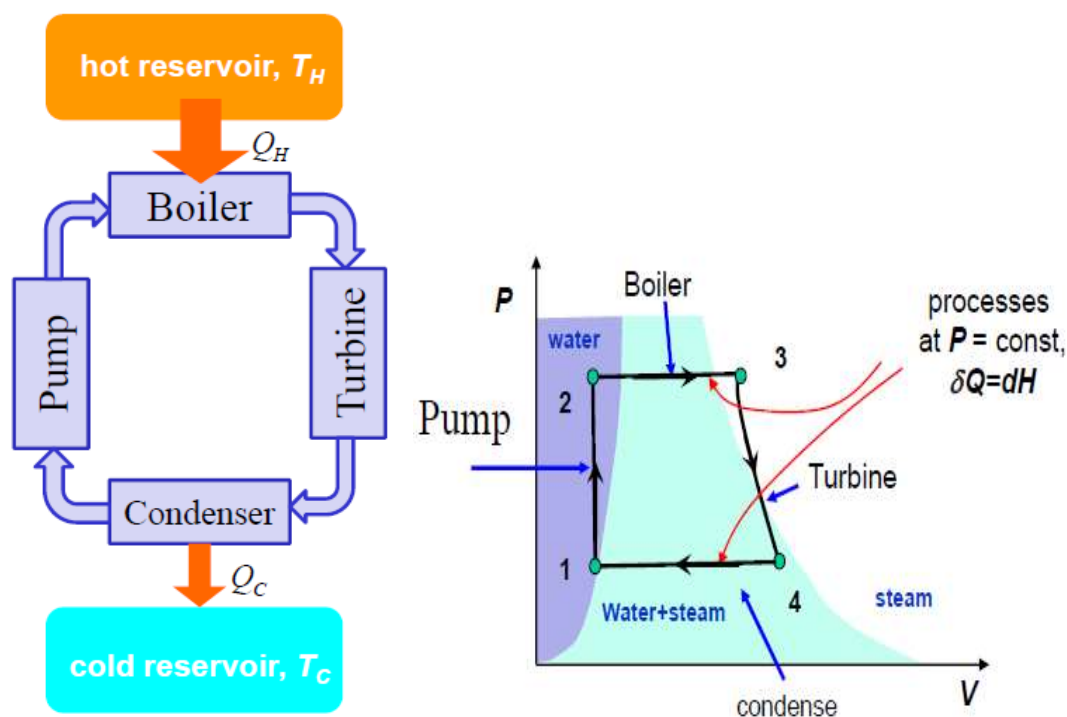
Figure 6.3 Schematic diagram of the Rankine (steam engine) along with its *PV* diagram

An important application of enthalpy is the Rankine cycle, which is an idealized cycle describing the steam engine. A schematic diagram of the cycle is shown in Figure 6.3, along with the PV diagram for the cycle. Starting at point 1, water is pumped to high pressure (point 2) and then flows into a boiler and then flows into a boiler, where heat is added at constant pressure. At point 3, the steam hits the turbine, where it expands adiabatically, cools, and ends up at the original low pressure (point 4). Finally, the partially condensed fluid is cooled further in a "condenser" (a network of pipes that are in good thermal contact with the low-temperature reservoir).

The working substance in a steam engine is definitely *not* an ideal gas since it condenses into a liquid during the cycle. Because of this complicated behavior, there's no way to calculate the efficiency of the cycle straight from the *PV* diagram. We can use the concept of enthalpy to determine the efficiency of the engine. In the Rankine cycle, heat is absorbed at constant pressure in the boiler and expelled at constant pressure in the condenser, so we can write the efficiency as

$$e_{rankine} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{H_4 - H_1}{H_3 - H_2} \approx 1 - \frac{H_4 - H_1}{H_3 - H_1}$$

The last approximation, $H_2 \approx H_1$, is pretty good because the pump adds very little energy to the water, while the PV term in H is very small for liquids in comparison to gases. Since the expansion of steam in turbine is approximately adiabatic, then $S_3 \approx S_4$. This implies that the percentage x of steam in the condenser is given by

$$S_3{}^{gas} = xS_4{}^{gas} + (1-x)S_4{}^{liquid} \Rightarrow H_4 = xH_4{}^{gas} + (1-x)H_4{}^{liquid}$$

Therefore, in order to determine the efficiency of the Rankine cycle, we need to determine H_1 (the enthalpy of the liquid water at the beginning of the Rankine cycle), H_3 (the enthalpy of the superheated steam at the end of the boiling phase), and H_4 (the enthalpy of water-steam mixer when it enters the condenser).

T (°C)	P (bar)	H_{water} (kJ)	H_{steam} (kJ)	S_{water} (kJ/K)	S_{steam} (kJ/K)
0	0.006	0	2501	0	9.156
10	0.012	42	2520	0.151	8.901
20	0.023	84	2538	0.297	8.667
30	0.042	126	2556	0.437	8.453
50	0.123	209	2592	0.704	8.076
100	1.013	419	2676	1.307	7.355

		Temperature (°C)				
P (bar)		200	300	400	500	600
1.0	H (kJ)	2875	3074	3278	3488	3705
	S (kJ/K)	7.834	8.216	8.544	8.834	9.098
3.0	H (kJ)	2866	3069	3275	3486	3703
	S (kJ/K)	7.312	7.702	8.033	8.325	8.589
10	H (kJ)	2828	3051	3264	3479	3698
	S (kJ/K)	6.694	7.123	7.465	7.762	8.029
30	H (kJ)		2994	3231	3457	3682
	S (kJ/K)		6.539	6.921	7.234	7.509
100	H (kJ)			3097	3374	3625
	S (kJ/K)			6.212	6.597	6.903
300	H (kJ)			2151	3081	3444
	S (kJ/K)			4.473	5.791	6.233

Figure 6.4 (Left) Properties of saturated water/steam. (Right) Properties of superheated steam. Copyright ©2000 Addison Wesley

Two different tables, shown in Figure 6.4, are generally used to look up the needed values of H. The first is for "saturated" water and steam, covering any point between the dashed lines on the PV diagram, where the temperature is determined by the pressure. This table lists the enthalpy and entropy for pure water and for pure steam at the boiling point; for mixtures of water and steam one can interpolate between these two values. The other table needed is for "superheated" steam, in the right-most region of the PV diagram where the pressure and temperature must be specified separately. Again, the table lists the enthalpy and entropy at each point.

Example 1

Suppose the cycle operates between a minimum pressure of 0.023 bar (where the boiling temperature is 20°C) and a maximum pressure of 300 bars, with a maximum superheated steam temperature of 600°C. Determine the efficiency of this steam engine.

143

Use Table 6.4, we note that $H_1 = 84\ kJ$, $H_3 = 3444\ kJ$, and $S_3 = 6.233\ kJ/K$. Since $S_4 = S_3$, then we can find the percentage of liquid water in the condenser by

$$xS_{water} + (1 - x)S_{steam} = 6.233\frac{kJ}{K} \Rightarrow x = 0.2908$$

Thus, in order to obtain the same entropy at point 4, we need a mixture of 29% water and 71% steam. This same mixture has an entropy of $H_4 = xH_{water} + (1 - x)H_{steam} = 1824\ kJ$. Therefore, the efficiency of this cycle is approximately

$$e = 1 - \frac{H_4 - H_1}{H_3 - H_1} = 1 - \frac{1824\ kJ - 84\ kJ}{3444\ kJ - 84\ kJ} = 48\%$$

6.1.3 The Refrigeration cycle

Recall that we defined a **refrigerator** as any thermodynamic cycle which transfers energy in the form of heat from a reservoir at a lower temperature to a reservoir at a higher temperature. A refrigerator carries some working substance through a cyclic process during which
1. The working substance absorbs energy from a low-temperature energy reservoir
2. Work is done on the engine
3. Energy is expelled by the engine to a higher-temperature reservoir

The **coefficient of performance** for a refrigerator is defined as

$$COP = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \left(\frac{Q_h}{Q_c} - 1\right)^{-1}$$

The Carnot theorem implies that the maximum COP for any refrigerator is given by

$$COP \leq COP_{max} = \left(\frac{T_H}{T_C} - 1\right)^{-1}$$

Thus, the COP is largest when $T_H \approx T_C$. For a typical kitchen refrigerator, $T_H \approx 300\ K$ and $T_C \approx 250\ K$, which produces $COP \approx 6$.
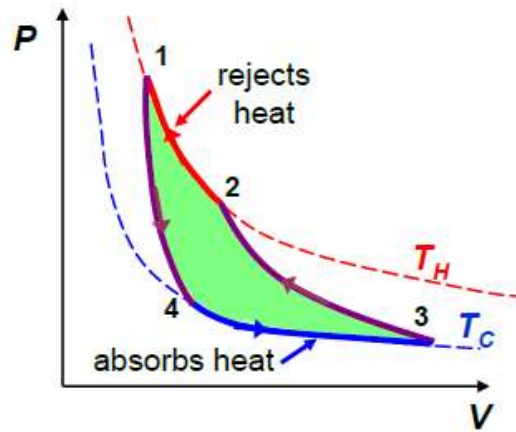
Figure 6.5 *PV* diagram of a Carnot refrigerator

We can create a refrigerator by running a Carnot engine backwards, as shown in Figure 6.5: the gas extracts heat from the cold reservoir and deposits it in the cold reservoir. However, it is difficult to build a practical refrigerator using a Carnot cycle since the energy absorbed per unit mass of working substance is relatively small. For this reason, real refrigerators use some liquid as a working substance.
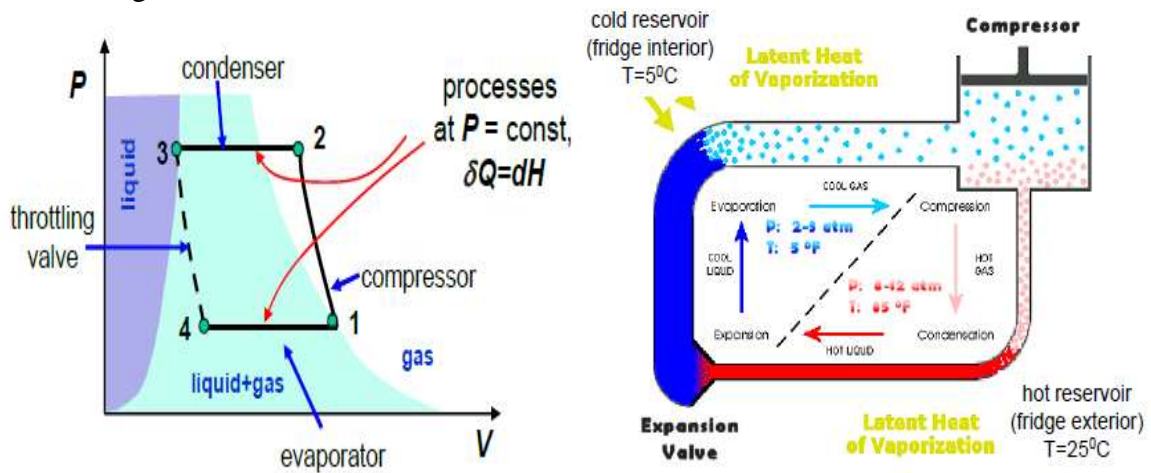
Figure 6.6 Schematic of a typical refrigerator with its *PV* diagram

The concept of enthalpy can also be used to describe the refrigeration process. The operation of an ordinary refrigerator (or air conditioner) is almost the reverse of the Rankine cycle just discussed. Again, the working substance changes back and forth from a gas to a liquid, but here the fluid must have a much lower boiling temperature. A schematic sketch and *PV* diagram of the standard refrigeration cycle is given in Figure 6.6. Beginning at point 1, the fluid (here a gas) is first compressed adiabatically, raising its pressure and temperature. It then gives up heat and gradually liquefies in the condenser (a network of pipes in thermal contact with the hot reservoir). Next it passes through a \textbf{throttling valve} -- a narrow opening or porous plug -- emerging on the other side at much lower pressure and temperature. Finally it absorbs

145

heat and turns back into a gas in the evaporator (a network of pipes in thermal contact with the cold reservoir. For a kitchen refrigerator, Freon circulates through the system. The compressor pushes the liquid through the condenser coil at a high pressure (~10 atm). The liquid sprays through a throttling valve into the evaporation coil which is maintained by the compressor at a low pressure (~2 atm).Because of the environmental impacts of Freon, refrigerants are replaced with HFC-134a

It's easy to express the coefficient of performance (COP) of a standard refrigerator in terms of the enthalpies of the fluid at various points around the cycle. Since the pressure is constant in the evaporator, the heat absorbed is $Q_c = H_1 - H_4$. Similarly, the heat expelled in the condenser is $Q_h = H_2 - H_3$. So the coefficient of performance is

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{H_1 - H_4}{H_2 - H_3 - H_1 + H_4}$$

To determine H_4, we must analyze the throttling process.

Expansion valve
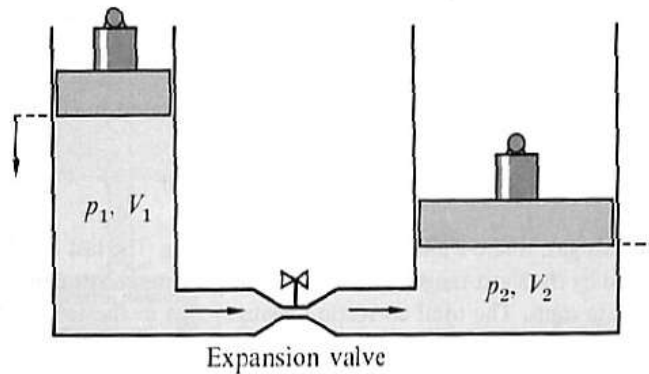
Figure 6.7 Schematic of the trottling process

The trottling process (also known as the **Joule-Thompson process**) is shown in Figure 6.7. Here a gas is allowed to flow adiabatically and steadily from a region of constant high pressure to a region of constant low pressure through a porous plug. Since the flow occurs adiabatically, then $dU = \delta W$. To calculate the work that is done in passing from one side of the porous plug to the other, it is convenient to imagine that a volume V_h from the high pressure region is moved to occupy a volume V_l in the low pressure region by the action of two pistons as shown on the right of Figure 8.7 (generally a steady flow and constant pressures are maintained by pumps). For instance, to start with the piston on the right would be pressed against the plug $V_l = 0$ and a certain volume V_h of the gas would lie between the piston on the left and the porous plug. The pistons are then moved together quasi-statically to the right in such a way that the pressures in each region are kept constant, and by the end of this process, a volume V_h has passed from the left to the right of the porous plug. It is then easy to see that the work done by the gas in

146

the high pressure region is $-P_h V_h$ and in the low pressure region it is $P_l V_l$. It follows that the total work done by the gas is

$$W = -P_h V_h + P_l V_l$$

and the total change in internal energy because the gas was initially in the high pressure region and ends up in the low pressure region is

$$\Delta U = U_l - U_h$$

so by the first law (there is no energy transfer by heat)
$$U_l - U_h - P_h V_h + P_l V_l = 0 \Rightarrow U_l + P_l V_l = U_h + P_h V_h \Rightarrow H_l = H_h$$

nd the process is **isenthalpic** (i.e., the enthalpy of the gas remains unchanged).

The *purpose* of the throttling valve is to *cool* the fluid to below the temperature of the cold reservoir so it can absorb heat as required. If the fluid were an ideal gas, this wouldn't work at all since the enthalpy of an ideal gas is

$$H = U + PV = \frac{f}{2} NkT + NkT = \left(\frac{f}{2} + 1 \right) NkT$$

Thus, for an ideal gas, constant enthalpy would imply constant temperature. However, in a real gas or liquid, the energy U also contains a potential energy term due to the force between the molecules: $H = U_{pot} + U_{kin} + PV$. The force between any two molecules is weakly attractive at long distances and strongly repulsive at short distances. This leads to two opposing effects:

(1) At low temperature, the attraction dominates, which implies that $U_{pot} < 0$. As the pressure drops during throttling, the mean free path increases and the potential becomes less negative. To compensate for the increase of potential energy, the kinetic energy generally decreases, and the fluid cools

(2) At high temperatures, the repulsive force dominates as fast-moving molecules suffer hard collisions during which there is high U_{pot}. When gas expands, collision frequency decreases, causing $\Delta U_{pot} < 0$. To compensate for the decrease of potential energy, the kinetic energy generally decreases, and the fluid warms.

Under most (though not all) conditions, the attraction dominates and the fluid cools as desired. If we use the fact that $H_4 = H_3$ in the refrigeration cycle, the COP for the refrigeration cycle simplifies to

$$COP = \frac{H_1 - H_3}{H_2 - H_1}$$

The enthalpies can be found in standard tables and using the same methodologies as discussed for the Rankine cycle.

6.1.4 Joule-Thompson Coefficient

As mentioned above, there are conditions in which the Joule-Thompson process is a warming process. The sign of ΔT depends on initial T and P. The temperature at which the behavior of the gas changes from cooling to warming is called the **inversion temperature**. The inversion temperature can be determined upon knowledge of the **Joule-Thomson coefficient**, given by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

Inversion will occur when μ_{JT} vanishes. To determine the Joule-Thompson coefficient, we start with Pfaffian of H

$$dH = TdS + VdP$$

If we think of $S = S(P, T)$, then

$$dH = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]dP$$

During the Joule Thompson process, $dH = 0$ and thus, we can rewrite this as

$$0 = C_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]dP$$

Now, the Maxwell relation associated with Gibbs free energy is given by

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

which gives us

$$C_P dT = \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]dP \equiv [\beta T - 1]VdP$$

148

Differentiating with respect to pressure gives the Joule-Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\beta T - 1)$$

which is true regardless of the thermal equation of state. When $\mu_{JT} > 0$ ($\mu_{JT} < 0$), the gas will cool (warm) upon expansion. For the ideal gas, the coefficient of volume expansion is just $\beta = 1/T$, therefore $\mu_{JT} = 0$. This is to be expected since neither mechanism for a change of temperature is available to the ideal gas: (i) there are no molecular interactions, so no loss of kinetic energy in favor of potential energy and (ii) the molecules are point-like and there are no collisions, so no kinetic energy is ever temporarily stored as potential energy during collisions.

All real gases have two inversion temperatures: upper and lower inversion temperatures, as shown in Figure 6.8. In the range between the upper and lower inversion temperatures, the Joule-Thomson process cools the gas. Outside this range, the Joule-Thomson heats the gas
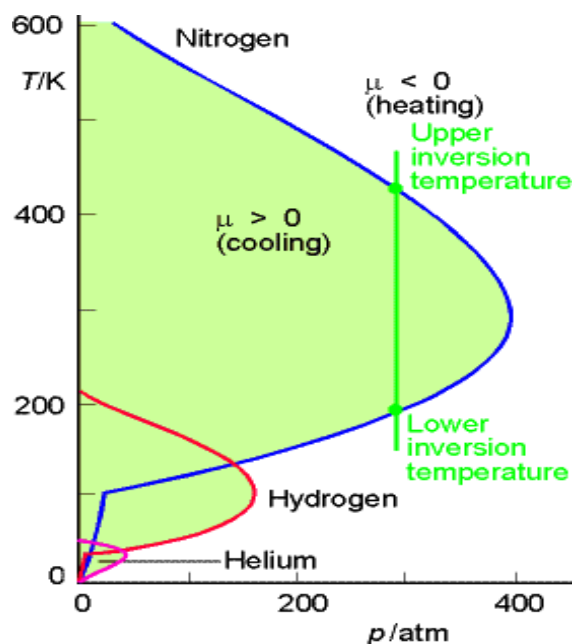
Figure 6.8 Pressure vs. temperature curve for hydrogen with upper and lower inversion temperature.

6.2 Helmholtz Free Energy

Recall from the previous chapter that Helmholtz free energy is defined as

$$F(T,V) = U(T,V) - TS(T,V)$$

The Pfaffian of $H(T,V)$ is given by

$$dF = -S\,dT - P\,dV$$

Based on the Pfaffian, we have

$$S(T,V) = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P(T,V) = -\left(\frac{\partial F}{\partial V}\right)_T$$

The Maxwell relation associated with enthalpy is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and finally the curvature of $F(T,V)$ is given by

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = \frac{1}{V\kappa_T} \qquad \left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\frac{C_V}{T}$$

What is the physical meaning of Helmholtz free energy? This can be answered in a number of ways. Recall that the enthalpy of a system was defined as the total energy of a system plus the work needed to place it in a given environment. Often, however, we're not interested in the total energy needed or the total energy that can be recovered. If the environment is isothermal, then the system can extract heat from this environment for free, so all we need to provide to create the system is the additional work needed. Similarly, if we completely remove the system, we generally cannot recover all is energy as work because we have to dispose of its entropy by dumping heat into the environment. Thus, Helmholtz free energy is the energy that must be provided as work in order to create a given thermodynamic system. We will examine this point in more detail in the next subsection.

6.2.1 Maximum Reversible Work

To see this, let's examine the change in the Helmholtz free energy. For an isothermal process, we have $dF = -P\,dV$. Thus, the *decrease* in the Helmholtz free energy is the work done by the system (this holds for reversible processes only). To see what would happen during an irreversible process we must return to the first law,

$$T \, dS \geq \delta Q = dU + P \, dV \Rightarrow d(TS) - S \, dT \geq dU + P \, dV \Rightarrow dF \leq -S \, dT - P \, dV$$

from which we see that during an isothermal process

$$P \, dV \leq -dF$$

Thus *the decrease in the Helmholtz free energy is an upper bound for the amount of work extracted from the system (done by the system)* (The work described here includes all work done by the system including any work done automatically by its expanding or collapsing environment). This is what gives this thermodynamic function its name, the "free energy". Only if the process is reversible is it possible to extract an amount of work equal to the decrease in free energy. In this sense, the free energy plays the role of the energy in mechanical systems, but it should be remembered that in mechanical systems the equality always holds. This point is worth reiterating

The decrease in the Helmholtz free energy is the maximum amount of work that can be obtained from a thermodynamic system (during isothermal processes)

In this way, Helmholtz free energy describes the available work of a thermodynamic system. However, Helmholtz free energy also describes the tendency of a system to approach thermodynamic equilibrium.

6.2.2 Minimum Free Energy and Equilibrium

Recall that for an isolated system, the entropy tends to increase and the system's entropy governs the direction of spontaneous change. Suppose that a system is in good thermal contact with its environment (and thus is no longer isolated). Now energy can pass between the system and the environment and, thus, the total entropy of the system plus its environment increases. Let's assume that the environment acts as a heat reservoir, large enough that it can absorb or release unlimited amounts of energy without changing its temperature. Therefore, the change in total entropy is

$$dS_{TOTAL} = dS + dS_R = \frac{dU}{T} + \frac{P}{T} dV + \frac{dU_R}{T_R}$$

Since only energy is exchanged between the system and its environment, then $dV = 0$. Moreover, since the total internal energy of the system and its environment is conserved, this implies that $dU_R = -dU$ and since the temperature of the reservoir doesn't change, then $T = T_R$

when the system reaches thermal equilibrium. This implies that the change in total entropy is given by

$$dS_{TOTAL} = dS - \frac{dU}{T} = -\frac{1}{T}(dU - TdS) = -\frac{dF}{T}$$

Therefore, under these conditions (fixed T and V), an increase in the total entropy of the universe (i.e. system plus environment) is the equivalent as a *decrease* in the Helmholtz free energy of the system. We conclude that, for isothermal systems involving no exchange of energy with the environment by mechanical work, the Helmholtz free energy of the system *may never increase*. It follows that **mechanically isolated systems operating at constant temperature achieve equilibrium at the minimum of the free energy**. This is a point worth repeating

The system's Helmholtz free energy minimizes when a system approaches equilibrium

Generally speaking, thermodynamic systems tend to minimize its Helmholtz free energy because when the system loses energy, its environment gains that energy, leading to an increase of the entropy in the environment. At low temperature, this effect tends to be transfer is large, proportional to $1/T$. But at high temperature, the environment doesn't gain as much entropy, so the entropy of the system becomes more important in determining the behavior of F.

6.2.3 The Helmholtz Free energy of an Ideal Gas

We can determine the Helmholtz free energy from an ideal gas based on knowledge of the entropy of an ideal gas. Writing $S = S(U,V)$ gives us

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{f}{2}Nk\frac{dT}{T} + Nk\frac{dV}{V}$$

where the final equality comes from the ideal gas law $PV = NkT$ and the internal energy of an ideal gas $U = (f/2)NkT$. Integrating gives us

$$S = S_0 + Nk\left[\frac{f}{2}\ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{V}{V_0}\right)\right]$$

Using the definition of Helmholtz free energy gives us

$$F = U - TS = \frac{f}{2}NkT - TS_0 + NkT\left[\frac{f}{2}\ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{V}{V_0}\right)\right]$$

If we choose $S_0 = 0$ and rearranging the above expression, we obtain

$$F = \frac{f}{2}NkT\left[1 - \ln\left(\frac{T}{T_0}\right) - \frac{2}{f}\ln\left(\frac{V}{V_0}\right)\right]$$

6.3 Gibbs Free Energy

Recall from the previous chapter that Gibbs free energy is defined as

$$G(T,P) = U(T,V) - TS(T,V) + PV(T,P)$$

The Pfaffian of $G(T,P)$ is given by

$$dG = -S\,dT + V\,dP$$

Based on the Pfaffian, we have

$$S(T,P) = -\left(\frac{\partial G}{\partial T}\right)_P, \qquad V(T,P) = \left(\frac{\partial G}{\partial P}\right)_T$$

The Maxwell relation associated with enthalpy is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

and finally the curvature of $G(T,P)$ is given by

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -V\kappa_T \qquad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{C_P}{T}$$

What is the physical meaning of Gibbs free energy? The Gibbs free energy G is related to the enthalpy H by: $G(T,P) = H(T,P) - TS(T,P)$. Recall that we defined the enthalpy as the total energy necessary to create a system and to place it in a given environment at constant pressure. If the environment is also at a constant temperature, then some of this energy can flow into the system spontaneously as work. Therefore, in order to create a closed thermodynamic system, the work required to make the system (at constant pressure) is the difference between the

total energy, H and the spontaneous flow of heat, TS. Thus, for system at constant temperature and pressure, $\Delta G = H - T\Delta S$.

6.3.1 Maximum Non-Expansion Work

The Gibbs free energy G is also related to the Helmholtz free energy F by G: $G(T,P) = F(T,P) + PV(T,P)$. Recall that we defined the Helmholtz free energy as the energy that must be provided as work in the creation of a thermodynamic system, where "work" means *all* work, including any that is done automatically by the system's surroundings. If the system is in an environment with constant pressure and temperature, then the work that must be provided to create the system is the Gibbs free energy G. Recall that the change in Helmholtz free energy is given by $\Delta F \leq W$ for any change in the system that takes place at constant temperature, where W includes *all* work done on the system, including any work done automatically by its expanding or collapsing environment. For any change that takes place at constant temperature and pressure (such as a phase transition), the change in G is

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V$$

If $W = W_{other} - P\Delta V$, then we have that $\Delta G \leq W_{other}$ for irreversible processes. Thus **the decrease in the Gibbs free energy is really an upper bound for the amount of non-expansion work extracted from the system.** This is a point worth emphasizing:

The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system
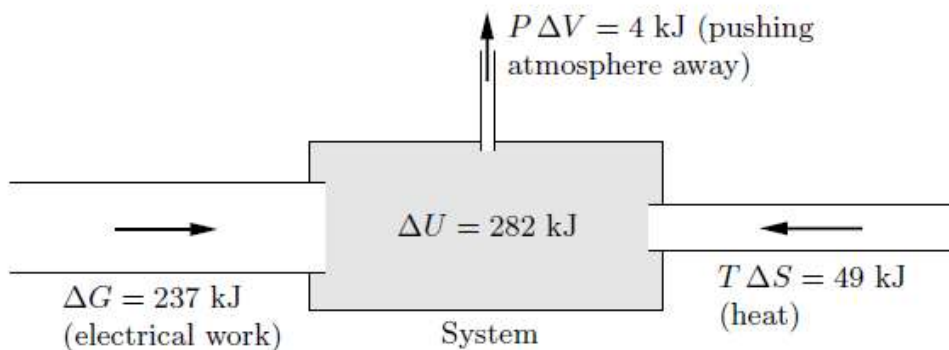
Figure 6.9 Energy-flow diagram for electrolysis of one mole of water

Consider the electrolysis of 1 mole of liquid water into hydrogen and oxygen gas

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$
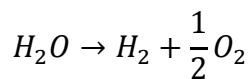
Standard reference tables show that $\Delta H = 286 \ kJ$ for this reaction, which implies that this is an endothermic reaction. Hence, when we form hydrogen and oxygen out of water, we need to put 286 kJ of energy into the system in some way or other. This is also the amount of heat you would obtain if you burning a mole of hydrogen, running the reaction in reverse. Out of the 286 kJ, a small amount goes into pushing the atmosphere away to make room for the gases produced; this amount is $P\Delta V = 4 \ kJ$. Of the 286 kJ needed, must we supply all the energy as work, or can some enter as heat? In other words, how much energy do we **actually** need to supply to complete this reaction? The amount of energy that must enter as electrical work is the change in Gibbs free energy. In this case, 237 kJ is the minimum work required to make the reaction go and 49 J of energy enters the system spontaneously through heat, as shown in Figure 6.9.

6.3.2 Minimum Free Energy and Equilibrium

We can also show that thermodynamic processes that approach equilibrium also tend to minimize the Gibbs free energy. Similar to our derivation for the minimization of F, suppose that a system is in good thermal contact with its environment (and thus is not isolated). If we assume that the environment acts as a heat reservoir and allow energy can pass between the system and environment, then the change in total entropy is

$$dS_{TOTAL} = dS + dS_R = \frac{dU}{T} + \frac{P}{T}dV + \frac{dU_R}{T_R}$$

Suppose we now allow the volume of the system to change, but keep it at the same pressure as the reservoir. Since the total internal energy and volume of the universe remains constant, this implies that $dU_R = -dU$ and $dV_R = -dV$. Since the temperature of the reservoir doesn't change, then $T = T_R$ when the system reaches thermal equilibrium. This implies that the change in total entropy is given by

$$dS_{TOTAL} = dS - \frac{dU}{T} + \frac{P}{T}dV = -\frac{1}{T}(dU - T \ dS + P \ dV) = -\frac{dG}{T}$$

Therefore, under these conditions (fixed T and P), an increase in the total entropy of the universe (i.e. system plus environment) is the equivalent as a *decrease* in the Gibbs free energy of the system. Similar to the Helmholtz free energy, thermodynamic systems tend to minimize its Gibbs free energy because when the system loses energy, its environment gains that energy, leading to an increase of the entropy in the environment. This is particularly important for processes during which both the pressure and the temperature remain constant, such as during a

phase transition. Therefore, **equilibrium in systems for which both the temperature and pressure remain constant is determined by the minimum of the Gibbs free energy**.

Our discussion of free energy leads to the following conclusions:
- At constant energy and volume, the entropy $S(U,V)$ tends to increase
- At constant temperature and volume, the Helmholtz free energy $F(T,V)$ tends to decrease
- At constant temperature and pressure, the Gibbs free energy $G(T,P)$ tends to decrease
- The Helmholtz free energy $F(T,V)$ gives the maximum work that can be extracted from a thermodynamic system
- The Gibbs free energy $G(T,P)$ gives the maximum non-PV work that can be extracted from a thermodynamic system

6.3.3 Gibbs Phase Rule

Recall the Pfaffian of G for a system with variable contents can be written as:

$$dG = -S\,dT + V\,dP + \mu dn$$

If we have a system with multiple types of particles, this can be generalized as

$$dG = -S\,dT + V\,dP + \sum_s \mu_s dn_s$$

This Pfaffian gives us a relationship between the Gibbs free energy and the chemical potential for a particular species

$$\mu_s(T,P,n_s) = \left(\frac{\partial G}{\partial n_s}\right)_{T,P} \Rightarrow G = \sum_s \mu_s n_s$$

The total differential for this expression is

$$dG = \sum_s \mu_s\,dn_s + \sum_s n_s d\mu_s$$

Comparing this expression to the Pfaffian of G gives

$$\sum_s n_s\,d\mu_s = -SdT + VdP$$

This is known as the **Gibbs-Duhem** relationship. It shows that in homogeneous systems the intensive variables are not really independent. When pressure and temperature vary only $s - 1$ of s species of substances present (in each phase) have independent chemical potentials.

This relationship has significant implications for multi-phase systems. Consider a system composed of p phases and n components (in other words, n is the number of chemically independent constituents of the system – i.e. the minimum number of independent chemical species necessary to define the composition of all phases of the system.). There are clearly a large number of potential variables describing this system, but not all of them are independent. The question is: how many of them can be independently chosen? What is the number of independent variables of the system? The answer is given by the **Gibbs phase rule**.

By the Gibbs-Duhem relation, the composition of each phase is determined by $n - 1$ intensive variables (i.e. composition terms) in each phase. For all phases, the total number of variables (excluding all constraints) is $(n - 1)p + 2$, where the extra "2" are temperature and pressure. These become the total number of our potential system variables. The number of constraints is $n(p - 1)$ since the chemical potential of each component must be equal in all phases. These become our fixed constraints for our given system. Thus, the number of independent intensive variables v (also known as the **degree of variability**) in our system is the total number of variables minus the constraints. Therefore, we have

$$v = [(n - 1)p + 2] - [n(p - 1)] = n - p + 2$$

Let's consider some examples of the usefulness of the Gibbs phase rule.

- For a system consisting of one phase and one chemically well-defined substance, $v = 2$. This system has two degrees of freedom, which we could choose to be temperature and pressure. Thus, there must be an equation relating temperature and pressure to the other extensive variables in the system. This is the thermal equation of state: $P = P(T, V)$.

- For a system of two distinct, chemically well defined gases, $v = 3$. This system has three degrees of freedom, which we could choose to be temperature, pressure, and composition. Thus, there must be an equation relating temperature, pressure, and composition to the other extensive variables in the system. This is the thermal equation of state for each composition species of the system: $P = P(T, V, N)$.

- For a system of one chemically well-defined substance and two phases (the liquid vapor system we have just examined), $v = 1$. This system has only one degree of freedom in equilibrium which we could choose to be the temperature. Thus there must be an equation relating the pressure to the temperature: $P = P(T)$. In the next chapter, we will show that equation is the **Clausius-Clapeyron relation**.

- For a system of one chemically well-defined substance and three phases, $v = 0$. This system has no degrees of freedom, which indicates that the system can only exist at a fixed pressure and temperature. This point is called the **triple point** of the system.

The Gibbs phase rule indicates that multi-phase systems have smaller degrees of variability than single-phase systems. In the next chapter, we will use our understanding of the Gibbs phase rule to introduce the phase diagrams associated with pure substances.

6.4 Free Energy and Stability

We obtained the curvatures of the potentials in Sect. 5.4.2. and we were able to relate those curvatures to caloric and mechanical properties giving us the signs of those curvatures. What we do not yet have, however, is a general stability requirement involving also the cross partial derivatives of the potentials. That is we are lacking a full stability requirement for the form of the potentials.

Stability of real substances is reflected in the curvatures of the fundamental surface $U(S, V, n_s)$. These curvatures result in thermal and mechanical stability requirements for real substances reflected in limits on the values of the specific heats (C_P, C_V) and the compressibilities (κ_T, κ_S). Recall that the curvatures for the internal energy are given as

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0, \quad \left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0$$

This means that the general stability requirements are:

$$\left(\frac{\partial T}{\partial S}\right)_V > 0, \quad -\left(\frac{\partial P}{\partial V}\right)_S > 0$$

We now seek more general stability requirements based on the basic form of the fundamental surface. Particularly, we seek a relationship that will tie the curvatures to the mixed second partial derivative.

The fundamental surface curves upward along the U-axis and this is the general requirement of stability resulting from the second law. If we choose a general state (a point) on the fundamental surface, which we designate as a, and construct a plane tangent to the surface at that point, then *all* points on the fundamental surface will lie above the tangent plane at a. This situation is illustrated in Figure 6.10. In Figure 6.10, the surface we have selected is a convenient

surface for the illustration and is not the fundamental surface of any particular substance. We have also chosen the point a, at which the tangent plane is located, to be at the base of the surface for ease of illustration only. It is important only to realize that for any such tangent plane, constructed at any point on such a surface with an upward curvature, the surface will always lie above the plane – that is a line parallel to the U-axis from the surface $U(S, V)$ will always strike the tangent plane at a point below the surface.

Fundamental Surface
Points of U(S,V)

Line Λ_U(S,V,S$_a$,V$_a$)

Tangent Plane
Points of U'(S,V,S$_a$,V$_a$)
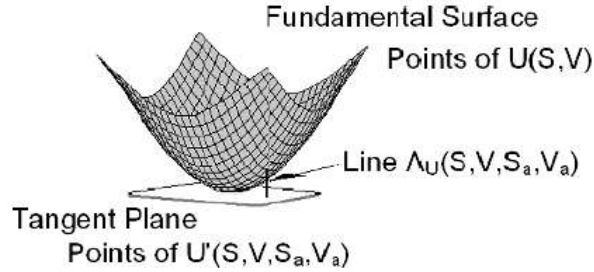
Figure 6.10 Fundamental surface with points $U(S, V)$ and a tangent plane with points $U'(S, V, S_a, V_a)$

We shall designate the points on the surface in Figure 6.10 as $U(S, V)$ and the points on the tangent plane as $U'(S, V; S_a, V_a)$. The points on the plane $U'(S, V; S_a, V_a)$ are specified by the function

$$U'(S, V; S_a, V_a) = U_a + \left[\left(\frac{\partial U'}{\partial S}\right)_V\right]_a (S - S_a) + \left[\left(\frac{\partial U'}{\partial V}\right)_S\right]_a (V - V_a)$$

$$= U_a + T_a(S - S_a) - P_a(V - V_a)$$

We now construct a line from the tangent plane to the fundamental surface. This line, which we call $\Lambda_U(S, V; S_b, V_b)$, is shown in Figure 6.10. Its length is the distance measured along the U-axis between the point on the fundamental surface $U(S, V)$ and the point on the tangent plane $U'(S, V; S_a, V_a)$. The length is given by

$$\Lambda_U(S, V; S_a, V_a) = U(S, V) - U'(S, V; S_a, V_a) = U(S, V) - U_a + T_a(S - S_a) - P_a(V - V_a)$$

For real substances, this length is positive because the fundamental surface is above the tangent plane – that is $\Lambda_U(S, V; S_a, V_a) > 0$.

We also construct a second plane tangent to the fundamental surface at a point (S_b, V_b) in the neighborhood of point (a). This is not shown in Figure 6.10. The points in this second plane we designate as $U''(S, V; S_b, V_b) = U_b + T_b(S - S_b) - P_a(V - V_b)$. We define a line between the fundamental surface and this plane just as we did for the tangent plane at the point a.

$$\Lambda_U(S,V;S_b,V_b) = U(S,V) - U'(S,V;S_b,V_b) = U(S,V) - U_b + T_b(S-S_b) - P_b(V-V_b) > 0$$
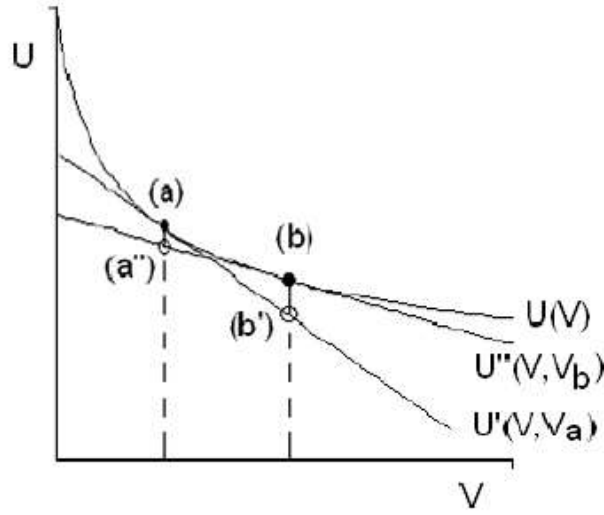
Figure 6.11 Projection of the fundamental surface onto a constant entropy plane. Tangent lines $U'(V,V_a)$ at (a) and $U''(V,V_b)$ at (b) are shown. These lie below the fundamental surface.

Because it is on the fundamental surface, the point (b) also lies above all points in the plane $U'(S,V;S_a,V_a)$. Likewise the point (a) lies above all points in the plane $U''(S,V;S_b,V_b)$. This situation is illustrated in Figure 6.11 where we have plotted the projection of the fundamental surface and the planes onto a constant entropy plane. On this plot, we have indicated two neighboring states (a) and (b) and drawn the tangent lines at these points with slopes $-P_a$ and $-P_b$. Points on these tangent lines are $U'(V,V_a)$ and $U''(V,V_b)$ respectively.

The distances $a''a$ and $b'b$ must both be positive. In terms of Λ_U, this is the requirement that

$$\Lambda_U(S_a,V_a;S_b,V_b) = U_a - U_b - T_b(S_a - S_b) + P_b(V_a - V_b) > 0$$
$$\Lambda_U(S_b,V_b;S_a,V_a) = U_b - U_a - T_a(S_b - S_a) + P_a(V_b - V_a) > 0$$

These inequalities are basic algebraic statements that must hold for any surface which lies above all of its tangent planes. This is the general geometric stability requirement for the fundamental surface and thus they are the basic stability requirements with which we shall work. Adding these expressions gives

$$\Delta T \Delta S - \Delta P \Delta V > 0 \qquad (6.1),$$

where $(\Delta T, \Delta S, \Delta V) = (T_b - T_a, S_b - S_a, V_b - V_a)$. Since $T = (\partial U/\partial S)_V$ and $P = -(\partial U/\partial V)_S$, then equation (6.1) is a relationship among the changes in the first derivatives (slopes) of the fundamental surface resulting from changes in the coordinates ΔS and ΔV.

If the states (a) and (b) are infinitesimally close we can use a linear Taylor series to write $\Delta T = (\partial U/\partial S)_V \Delta S$ and $\Delta P = -(\partial U/\partial V)_S \Delta V$. Then Equation (6.1) becomes

$$\left[\left(\frac{\partial T}{\partial S}\right)_V\right]_a \Delta S^2 - \left[\left(\frac{\partial P}{\partial V}\right)_S\right]_a \Delta V^2 > 0$$

where a is any arbitrary state point on $U(S,V)$. Therefore, Equation (6.1) is our curvature requirement in a general form.

We recall that in Sect. 5.2.4 we were able to deduce the curvatures of the potentials based on our claim that the specific heats and the compressibilities are positive. The claim was valid, but we presented no scientific evidence for the claim. Here we do present the necessary scientific evidence. We now seek a stability requirement based upon second derivatives. To introduce second derivatives, we carry out a Taylor expansion of the energies U_a and U_b to second order in ΔS and ΔV. The energy U_b is found from a second order Taylor expansion around a as

$$U_b = U_a + T_a(S_b - S_a) - P_a(V_b - V_a) + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V\right]_a \Delta S^2 + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S\right]_a \Delta V^2$$

$$+ \left[\left(\frac{\partial^2 U}{\partial S \partial V}\right)\right]_a \Delta S \Delta V$$

Similarly, U_a is found from a second order Taylor expansion around b as

$$U_a = U_b + T_b(S_a - S_b) - P_b(V_a - V_b) + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V\right]_b \Delta S^2 + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S\right]_b \Delta V^2$$

$$+ \left[\left(\frac{\partial^2 U}{\partial S \partial V}\right)\right]_b \Delta S \Delta V$$

Using our basic stability requirements $\Lambda_U(S_a, V_a; S_b, V_b) > 0$ and $\Lambda_U(S_b, V_b; S_a, V_a) > 0$, our above expressions can be reduced to

$$\frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V\right]_a \Delta S^2 + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S\right]_a \Delta V^2 + \left[\left(\frac{\partial^2 U}{\partial S \partial V}\right)\right]_a \Delta S \Delta V > 0$$

$$\frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V\right]_b \Delta S^2 + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial V^2}\right)_S\right]_b \Delta V^2 + \left[\left(\frac{\partial^2 U}{\partial S \partial V}\right)\right]_b \Delta S \Delta V > 0$$

Because the two points a and b are arbitrary, the above expressions are forms of the general inequality

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \Delta S^2 + \left(\frac{\partial^2 U}{\partial V^2}\right)_S \Delta V^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)\Delta S \Delta V > 0$$

that must be satisfied for any point on the fundamental surface. Since $(\partial^2 U/\partial S^2)_V > 0$ and $(\partial^2 U/\partial V^2)_S > 0$ for any real substance, we can multiply the above expression by $(\partial^2 U/\partial S^2)_V$ to obtain

$$\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V \Delta S + \left(\frac{\partial^2 U}{\partial V \partial S}\right)\Delta V\right]^2 + \left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial V \partial S}\right)^2\right](\Delta V)^2 > 0$$

Since the first term is always positive, this implies that our general stability requirement condition is

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial V \partial S}\right)^2 > 0 \qquad (6.2)$$

The left hand side of Equation (6.2) can be written as the determinant of the matrix

$$\begin{bmatrix} \left(\frac{\partial^2 U}{\partial S^2}\right)_V & \left(\frac{\partial^2 U}{\partial V \partial S}\right) \\ \left(\frac{\partial^2 U}{\partial V \partial S}\right) & \left(\frac{\partial^2 U}{\partial V^2}\right)_S \end{bmatrix} = \begin{bmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ -\left(\frac{\partial P}{\partial S}\right)_V & -\left(\frac{\partial P}{\partial V}\right)_S \end{bmatrix}$$

Therefore, our general stability condition is given by

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial V \partial S}\right)^2 = \det\begin{bmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ -\left(\frac{\partial P}{\partial S}\right)_V & -\left(\frac{\partial P}{\partial V}\right)_S \end{bmatrix} = -\det\begin{bmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ \left(\frac{\partial P}{\partial S}\right)_V & \left(\frac{\partial P}{\partial V}\right)_S \end{bmatrix}$$

$$= -\frac{\partial(T,P)}{\partial(S,V)} > 0$$

where $\partial(T,P)/\partial(S,V)$ refers to the *Jacobian matrix* of the transformation. Therefore, our general condition for thermodynamic stability of the fundamental surface $U(S,V)$ is

$$\frac{\partial(T,P)}{\partial(S,V)} < 0$$

A basic property of a Jacobian, which can be proved in multi-variable calculus text, is that

$$\frac{\partial(x_i, x_j)}{\partial(y_i, y_j)} = \left(\frac{\partial x_i}{\partial y_i}\right)_{x_j} \left(\frac{\partial x_j}{\partial y_j}\right)_{y_i}$$

Applying this condition to our stability requirement gives

$$\frac{\partial(T,P)}{\partial(S,V)} = \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_T < 0$$

The above expression provides forms of the stability requirement that can be applied readily to other potentials. For example, note that

$$\frac{\partial(T,P)}{\partial(S,V)} = \left(\frac{\partial(S,V)}{\partial(T,P)}\right)^{-1} < 0$$

Now, the stability requirement can be written in terms of Gibbs free energy:

$$\frac{\partial(S,V)}{\partial(T,P)} = \det\left[\begin{matrix} \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{matrix}\right] = \det\left[\begin{matrix} -\left(\frac{\partial^2 G}{\partial T^2}\right)_P & -\left(\frac{\partial^2 G}{\partial P \partial T}\right) \\ \left(\frac{\partial^2 G}{\partial T \partial P}\right) & \left(\frac{\partial^2 G}{\partial P^2}\right)_T \end{matrix}\right] < 0$$

$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2}\right)_P \left(\frac{\partial^2 G}{\partial P^2}\right)_T - \left(\frac{\partial^2 G}{\partial P \partial T}\right)^2 > 0$$

$$\Rightarrow \frac{C_P}{T}\kappa_T - \beta^2 V > 0$$

Since we know that the mechanical response functions are connected to the caloric response functions by,

$$C_P - C_V = T\frac{\beta^2 V}{\kappa_T}$$

Then our stability condition is given by

$$\frac{\left(C_V + T\frac{\beta^2 V}{\kappa_T}\right)}{T}\kappa_T - \beta^2 V = \frac{C_V}{T} > 0 \Rightarrow C_V > 0$$

This means that the requirement that the specific heat at constant volume is a positive quantity is a consequence of thermodynamics, not a requirement imposed on thermodynamics.

6.4 Summary of the Thermodynamic Potentials

As mentioned in the introduction to this chapter, a principle goal of classical thermodynamics is to find the point of view from which the mathematical combination of the law of thermodynamics appears in its simplest form. This chapter has demonstrated that consequences of the laws of thermodynamics are completely contained in the geometry of a single fundamental surface written in terms of five thermodynamic potentials: internal energy $U(S,V)$, entropy $S = S(U,V)$, enthalpy $H = H(S,P)$, Helmholtz free energy $F = F(T,V)$, and Gibbs free energy $G = G(T,P)$. Furthermore, in generalizing our discussion to include thermodynamic systems with variable contents, we introduced the chemical potential μ, which can be thought of as the Gibbs free energy per particle.

Each potential is an extensive variable that acquires a special meaning for particular thermodynamic processes. Internal energy U is all the energy of a system (translational kinetic energy; rotational kinetic kinetic energy; vibrational kinetic energy; and potential energy; etc.) associated with its elementary constituents when viewed from a reference frame at rest with respect to the object. Enthalpy H is the total energy associated with a thermodynamic system, as well as the work necessary to place it in a given environment at constant pressure. It is generally useful in describing isobaric processes and refrigeration processes specifically. Helmholtz free energy F (more specifically, the decrease in F) is the total useful or available work that can be extracted from a closed thermodynamic system at constant temperature and it is generally useful for describing equilibrium processes that occur at constant volume. Gibbs free energy (more specifically, the decrease in G) is the maximum amount of non-expansion work that can be extracted from a closed system at a constant temperature. In the next chapter, we will discuss the primary use for the Gibbs free energy: phase transformations.

Below we give a summary of the major results associated with each thermodynamic function. The Pfaffians of each thermodynamic potential in terms of their characteristic variables are given by

$$dU = TdS - PdV + \sum_s \mu_s dN_s$$
$$dH = TdS + VdP + \sum_s \mu_s dN_s$$
$$dF = -SdT - PdV + \sum_s \mu_s dN_s$$

$$dG = -SdT + VdP + \sum_s \mu_s dN_s$$

The generalized forces associated with thermodynamic potential are given by

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_s} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N_s} = -P, \quad \left(\frac{\partial U}{\partial N_s}\right)_{S,V,N_r,r\neq s} = \mu_s$$

$$\left(\frac{\partial H}{\partial S}\right)_{P,N_s} = T, \quad \left(\frac{\partial H}{\partial P}\right)_{S,N_s} = V, \quad \left(\frac{\partial H}{\partial N_s}\right)_{S,P,N_r,r\neq s} = \mu_s$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N_s} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N_s} = -P, \quad \left(\frac{\partial F}{\partial N_s}\right)_{T,V,N_r,r\neq s} = \mu_s$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N_s} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T,N_s} = V, \quad \left(\frac{\partial G}{\partial N_s}\right)_{T,P,N_r,r\neq s} = \mu_s$$

The Maxwell relations associated with each thermodynamic potential is given

$$\left(\frac{\partial T}{\partial V}\right)_{S,N_s} = -\left(\frac{\partial P}{\partial S}\right)_{V,N_s}, \quad \left(\frac{\partial T}{\partial N_s}\right)_{V,S,N_r,r\neq s} = \left(\frac{\partial \mu_s}{\partial S}\right)_{V,N_s}, \quad \left(\frac{\partial P}{\partial N_s}\right)_{V,S,N_r,r\neq s} = \left(\frac{\partial \mu_s}{\partial V}\right)_{S,N_s}$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,N_s} = \left(\frac{\partial V}{\partial S}\right)_{P,N_s}, \quad \left(\frac{\partial T}{\partial N_s}\right)_{V,S,N_r,r\neq s} = \left(\frac{\partial \mu_s}{\partial S}\right)_{P,N_s}, \quad \left(\frac{\partial V}{\partial N_s}\right)_{P,S,N_r,r\neq s} = \left(\frac{\partial \mu_s}{\partial P}\right)_{S,N_s}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,N_s} = \left(\frac{\partial P}{\partial T}\right)_{V,N_s}, \quad \left(\frac{\partial S}{\partial N_s}\right)_{V,T,N_r,r\neq s} = -\left(\frac{\partial \mu_s}{\partial T}\right)_{V,N_s}, \quad \left(\frac{\partial P}{\partial N_s}\right)_{V,T,N_r,r\neq s} = -\left(\frac{\partial \mu_s}{\partial V}\right)_{T,N_s}$$

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N_s} = \left(\frac{\partial V}{\partial T}\right)_{P,N_s}, \quad \left(\frac{\partial S}{\partial N_s}\right)_{P,T,N_r,r\neq s} = -\left(\frac{\partial \mu_s}{\partial T}\right)_{P,N_s}, \quad \left(\frac{\partial V}{\partial N_s}\right)_{P,T,N_r,r\neq s} = \left(\frac{\partial \mu_s}{\partial P}\right)_{T,N_s}$$

Chapter 7: Multi-Phase Systems

Up to now, we have dealt almost exclusively with systems consisting of a single **phase**. A **phase** can be defined as a homogeneous mixture, in a definite physical state, of all possible chemical compounds that can be formed from the chemical elements present. The thermodynamic properties of any given phase of a substance will depend on T, P and the relative concentrations of all the elements. In this chapter, we will learn how more complicated, multi-phase systems can be treated by the methods of thermodynamics learned in previous chapters. We will see that the guiding principle will be the minimization of the Gibbs free energy in equilibrium for all systems.

7.1 Overview of Phase Diagrams
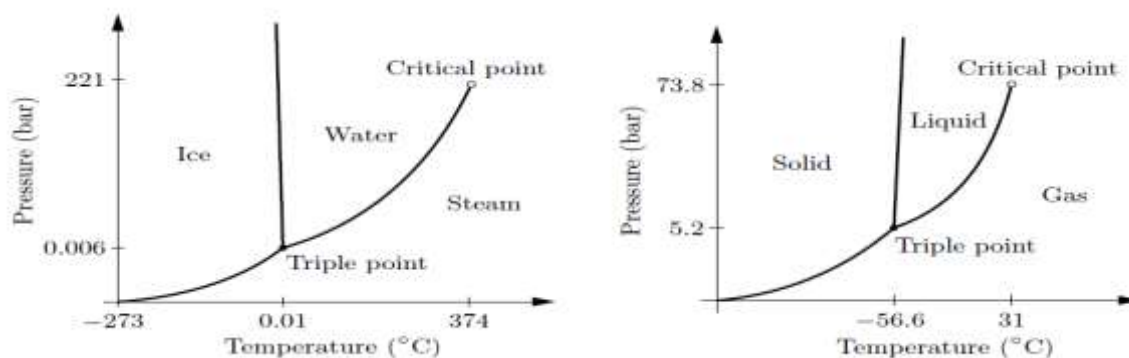
Figure 7.1 (a) Phase diagram for H_2O. (b) Phase diagram for CO_2.

A **phase transformation** is a discontinuous change in the properties of a substance, as its environment is changed only infinitesimally. Familiar examples include melting ice and boiling water, either of which can be accomplished with only a small change in temperature. Often there is more than one variable that can affect the phase of a substance. For instance, you can condense steam either by lowering the temperature or by raising the pressure. A graph showing the equilibrium phases as a function of temperature and pressure is called a **phase diagram**.

Figure 7.1(a) shows a qualitative phase diagram for pure water. The diagram is divided into three regions indicating the conditions under which ice, water, or steam is the most stable phase (i.e. the conditions under which ice, water, or steam has the lowest Gibbs free energy). It's important to note that "metastable" phases can still exist; for instance, liquid water can be "supercooled" below the freezing point yet remain a liquid for some time. Moreover, at high pressures, there are actually several different phases of ice, with differing crystal structure and other physical properties.

The lines on a phase diagram represent conditions under which two different phases can coexist in equilibrium and thus are called **coexistence curves**. Consistent with the Gibbs' phase rule, we note that the functional form of the coexistence curves is $P = P(T)$. For instance, ice and water can coexist stably at $0°C$ and 1 atm. The pressure at which a gas can coexist with its solid or liquid phase is called the **vapor pressure**. At $T = 0.01°C$ and $P = 0.006$ atm, all three phases can coexist; this point is called the **triple point of water**. The system undergoes phase transformation each time we cross the equilibrium curves.

A qualitative phase diagram for carbon dioxide is shown in Figure 7.1b. One difference between carbon dioxide and water is that the triple point of carbon dioxide lies above atmospheric pressure (close to 5.2 atm). Another difference between carbon dioxide and water is the slope of the solid-liquid phase boundary. Most substances behave like carbon dioxide in that applying more pressure **raises** its melting temperature. However, ice is unusual in that applying pressure **lowers** its melting temperature. This is a result of the fact that ice is less dense than water. This behavior can be understood by examining the Pfaffian of G:

$$dG = -SdT + VdP + \sum_s \mu_s dn_s$$

The pressure dependence of the Gibbs free energy is given by

$$V(T, P, n_s) = \left(\frac{\partial G}{\partial P}\right)_{T, n_s}$$

Thus, the volume determines the pressure dependence of the Gibbs free energy. For most substances, such as carbon dioxide, the molar volume of the solid phase is smaller than the molar volume of the liquid phase. This would cause the solid phase to have the smaller Gibbs free energy, causing the solid phase to be in stable equilibrium at higher pressures. Therefore, a positive solid-liquid phase boundary indicates that the solid phase will be in stable equilibrium at higher pressures and increasing the pressure would raise the melting temperature. Unlike most substances, the molar volume of ice is larger than the molar volume of liquid water. This would cause the liquid phase to have the smaller Gibbs free energy, causing the liquid phase to be in stable equilibrium at higher pressures. Therefore, a negative solid-liquid phase boundary indicates that the liquid phase will be in stable equilibrium at higher pressures and increasing the pressure would decrease the melting temperature.

However, the liquid-gas phase boundary always has a positive slope: If you have liquid and gas in equilibrium and you raise the temperature, you must apply *more* pressure to prevent vaporization. As the pressure increase, the gas becomes more dense, so the difference between

liquid and gas grows less. Eventually a point is reached where there is no longer any discontinuous change from liquid to gas. This point is called the **critical point**, and occurs at $374°C$ and 221 atm for water. The critical point of carbon dioxide is more accessible at $31°C$ and 74 atm, while that of nitrogen is at only 126 K and 34 atm. There's no critical point on the solid-liquid phase boundary, since the distinction between solids and liquids is a qualitative issue (solids having crystal structure and liquids having randomly arranged molecules), not just a matter of degree.

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \rightarrow \infty$$
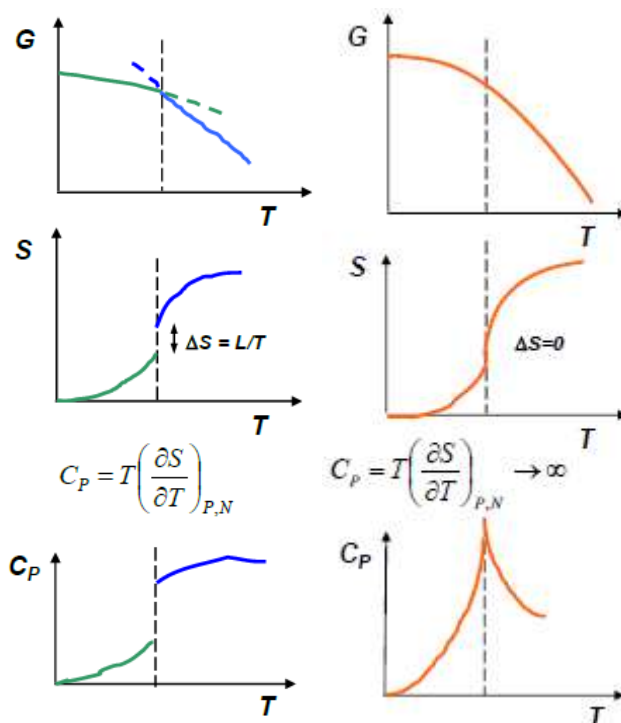
Figure 7.2 The Gibbs free energy, entropy, and heat capacity at constant pressure as a function of temperature for a first-order phase transition (left) and second-order phase transition (right).

The discussion of the critical point leads to an important distinction concerning phase transitions. The transitions which display a jump in entropy and a latent heat associated with this jump are called the **first-order phase transitions.** Because molecules aggregated differently in different phases, we have to provide (or remove) energy when crossing the coexistence curves. Latent heat is this energy difference and crossing the coexistence curve causes the system to release (or absorbs) latent heat and thus, the entropy of the system changes abruptly. The temperature driven phase transition that occurs exactly at the critical point is called a **second-order phase transition**. Unlike the first order transitions, the second order transition does not require any latent heat. In the higher order transitions, the entropy is continuous across the transition and the specific heat diverges at the transition.
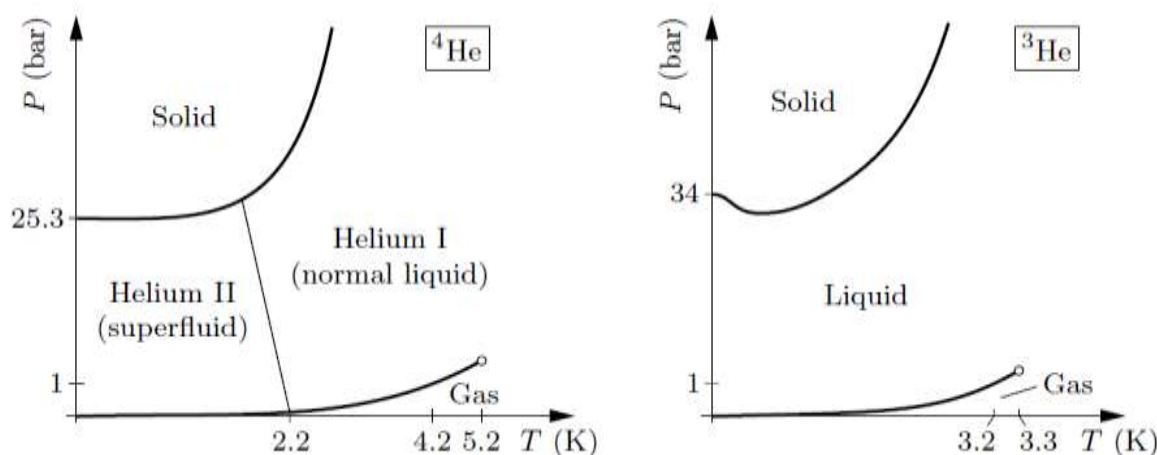
Figure 7.3 Qualitative phase diagrams of ^4He (left) and ^3He

Helium has the most exotic phase behavior of any element. Figure 5.2 shows the phase diagrams of the two isotopes of helium, the common isotope ^4He and the rare isotope ^3He. The boiling point of ^4He at atmospheric pressure is only 4.2 K, and the critical point is only slightly higher, at 5.2 K and 2.3 bars; for ^3He these parameters are somewhat lower still. Helium is the only element that remains a liquid at absolute zero temperature: It *will* form a solid phase, but only at rather high pressures, about 25 bars for ^4He and 30 bars for ^3He. The solid-liquid phase boundary for ^4He is almost horizontal below 1 K, while for ^3He this boundary has a *negative* slope below 0.3 K. Even more interesting, ^4He has two distinct liquid phases: a "normal" phase called **helium I**, and a superfluid phase, below about 2 K, called **helium II**. The superfluid phase has a number of remarkable properties including zero viscosity and very high thermal conductivity. We will discuss more about the properties of helium in the next section

Elemental carbon has two familiar phases: diamond and graphite (both solids, but with different crystal structures). At ordinary pressures the more stable phase is graphite, so diamonds will spontaneously convert to graphite, although this process is extremely slow at room temperature. The fact that graphite is more stable than diamond under standard conditions is reflected in their Gibbs free energies: The Gibbs free energy of a mole of diamond is greater, by 2900 J, than the Gibbs free energy of a mole of graphite. However, a molar volume of graphite is larger than the molar volume of diamond. Thus, since $V(T, P, n_s) = (\partial G / \partial P)_{T,n_s}$, the Gibbs free energy for graphite will grow more rapidly as the pressure is raised.
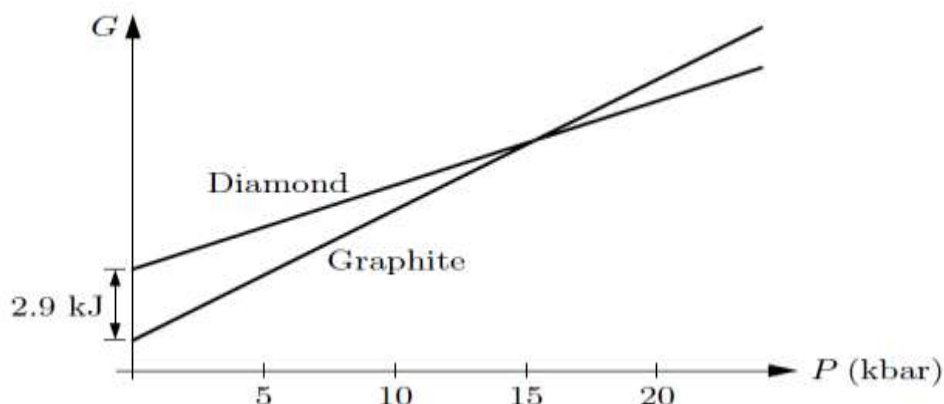
Figure 7.4 Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

Figure 7.4 shows a graph of G vs. P for both substances. If we treat the volumes as constant (neglecting the compressibility of both substances), then each curve is a straight line. As the figure shows, the two lines intersect at a pressure of about 15 kilobars, and above this pressure, diamond should be more stable than graphite. This implies that natural diamonds must form at very great depths.

The temperature dependence of the Gibbs free energies can be determined in a similar way, using the thermodynamic identity associated with G

$$S(T, P, n_s) = -\left(\frac{\partial G}{\partial T}\right)_{P, n_s}$$

As the temperature is raised the Gibbs free energy of either substance decreases, but this decrease is more rapid for graphite since it has more entropy. Thus, raising the temperature tends to make graphite more stable relative to diamond; the higher the temperature, the more pressure is required before diamond becomes the stable phase.

7.2 Clausius-Clapeyron Relation

According to the Pfaffian of G, the entropy determines the temperature dependence of the Gibbs free energy, while volume determines its pressure dependence. This implies that the shape of any phase boundary on a phase diagram is related in a very simple way to the entropies and volume of the two phases. This is called the **Clausius-Clapeyron relation** and we will derive this relation.

For definiteness, let's consider the liquid-gas phase boundary (although the results are general to any phase boundary). At the phase boundary, the Gibbs free energy must be the same, whether it is in either phase: $G_l = G_g$. You can also think of this condition in terms of the chemical potentials. If some liquid and some gas are in diffusive equilibrium with each other, then their chemical potentials, i.e. Gibbs free energies per molecule, must be equal. Now suppose that we increase the temperature by dT and the pressure by dP, in such a way that the two phases remain equally stable (i.e. remain on the phase boundary). Under this change, the Gibbs free energies must remain equal to each other so $dG_l = dG_g$. Therefore, by the Pfaffian for G,

$$-S_l dT + V_l dP + \mu_l dn_l = -S_g dT + V_g dP + \mu_g dn_g$$

Since the total number of molecules remains the same along the phase boundary and the chemical potential in each phase are equal, we have

$$-S_l dT + V_l dP = -S_g dT + V_g dP$$

Solving for the slope of the phase boundary line dP/dT gives

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S}{\Delta V}$$

As expected, the slope of the phase boundary is determined by the entropies and volumes of the two phases. A large difference in entropy means that a small change in temperature can be very significant in shifting the equilibrium from one phase to the other. This results in a steep phase boundary curve, since a large pressure change is then required to compensate for the small temperature change. On the other hand, a large difference in volume means that a small change in pressure can be significant after all, making the phase boundary curve shallower.

It's often more convenient to write the difference in entropies, $\Delta S = S_g - S_l$, as $L(T)$, where L is the total latent heat for converting the material from liquid to gas (which is usually a function of temperature). Therefore, the slope of the phase boundary line takes the form

$$\frac{dP}{dT} = \frac{L(T)}{T \Delta V}$$

This result is known as the **Clausius-Clapeyron relation** and it applies to the slope of **any** phase boundary line on a phase diagram. Essentially, the Clausius-Clapeyron relation tells us that the temperature dependence of the latent heat determines the slope of the phase boundary. Here are some examples which demonstrate the utility of this relationship.

Example 1: Diamond and Graphite Consider again the diamond-graphite system. When a mole of diamond converts to graphite its entropy increases by 3.4 J/K, while its volume increases by 1.9×10^{-6} m³. (both of these numbers are for room temperature). Therefore the slope of the diamond-graphite phase boundary is

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{3.4 \, J/K}{1.9 \times 10^{-6} \, m^{-3}} = 18 \frac{bar}{K}$$

Previously, we showed that at room temperature, diamond is stable at pressures above approximately 15 kbar. Now we see that if the temperature is 100 K higher than room temperature, we need an additional 1.8 kbar of pressure to make diamond stable. *Rapid* conversion of graphite to diamond requires still higher temperatures, and correspondingly higher pressures. The first synthesis of diamond from graphite was accomplished at approximately 1800 K and 60 kbar. Natural diamonds are thought to form at similar pressures but somewhat lower temperatures, at depths of 100 – 200 km below Earth's surface.

Example 2: Helium-3 As another example of the usefulness of the Clausius-Clapeyron relation, consider the phase diagram of ^3He in Figure 7.3. As mentioned previously, the slope of the solid-liquid boundary of ^3He is negative. According to the Clausius-Clapeyron relation, this implies that ΔS and ΔV have opposite signs. Therefore, during a transition from liquid ^3He to solid ^3He, the volume decreases, leading to an increase of entropy. This means that solid ^3He has higher entropy than liquid ^3He. Since $\Delta S = L(T)/T$, this implies heat is absorbed from the liquid phase to change liquid ^3He to solid ^3He, which is the opposite of virtually all elements. This states that it's possible to cool the liquid phase of ^3He through compression. As the solid-liquid mixture is compressed, heat is removed from the liquid phase as crystals form. This method of cooling ^3He was first suggested by I. Y. Pomeranchuk in 1950 and is called **Pomeranchuk cooling**. This method of cooling has been used with great success as a method of reaching temperatures as low as 1 mK.

Example 3: H_2O As another example, consider the phase diagram of H_2O in Figure 7.1. Just as in ^3He, the solid-liquid boundary of H_2O is negative. As ice melts into water, the change in entropy is positive, while the change in volume is negative. The negative slope of the solid-liquid coexistence curve makes ice skating possible. Ice melts under the pressure exerted by the skate blade, making ice slippery (for a more detailed view of this point, see the following article: http://lptms.u-psud.fr/membres/trizac/Ens/L3FIP/Ice.pdf). The Clausius-Clapeyron equation provides the connection between ice skating and the observation that ice floats on water.

The Clausius-Clapeyron relation is a differential equation that, in principle, can be solved to find the shape of the the entire phase-boundary curve of a given substance. To solve it, however, you have to know how both L and ΔV depend upon temperature of pressure. Often,

over a reasonably small section of the curve, you can take L to be constant, independent of temperature and pressure. Moreover, if one of the phases is a gas, you can usually neglect the volume of the condensed phase since $V_l \ll V_g$ and just take $\Delta V \approx V_g$, expressed in terms of temperature and pressure using the ideal gas law. Making these assumptions, the Clausius-Clapeyron relation becomes

$$\frac{dP}{dT} = \frac{L(T)}{T\Delta V} \approx \frac{L}{TV_g} = \frac{LP}{RT^2}$$

Solving this equation gives

$$P = P_0 \exp\left[-\frac{L}{RT}\right]$$

This result is the **vapor pressure equation**. This expression indicates that the pressure necessary to keep liquid (or solid) in equilibrium with gas increases with temperature. For this reason, this pressure is called the **equilibrium vapor pressure** or the **saturation vapor pressure**. The vapor pressure equation can be used to estimate the boiling point of various substances, including water. **The boiling point** is defined as the temperature at which the equilibrium vapor pressure of a liquid is equal to the surrounding atmospheric pressure. Since the vapor pressure varies with temperature according to the vapor pressure equation, the boiling point is a function of pressure.

7.2.1 Moist Convection

Suppose we have an air mass rising adiabatically in the atmosphere. As the air parcel rises, the atmospheric pressure exerted on the parcel decreases. If we assume that the pressure within the air mass remains constant, this implies that the air mass will expand. According to the first law of thermodynamics, this expansion will lead to a decrease in internal energy since $dU = -P\,dV$ for an adiabatic process. Thus, the expansion of the air mass occurs at the expense of its internal energy. Therefore, as an air parcel rises, it will expand and cool. The condition for convection to occur is that the rising air mass must *remain* warmer than the surrounding air despite this adiabatic cooling. This process leads to the following important question: what is the threshold temperature gradient needed in order for convection to spontaneously occur?

We first considered this question for unsaturated air and then generalize this procedure for moist air. Using the first law for an adiabatic process and the barometric equation, we saw that

$$-\frac{dT}{dz} = \frac{2}{f+2}\frac{Mg}{R}$$

Since $M = 29\ g/mol$ is the molar mass of dry air and since air is composed primarily of diatomic molecules (78% N_2 and 20% O_2), then $f = 5$ and the critical temperature gradient is given by

$$\Gamma_d \equiv -\frac{dT}{dz} = -\frac{2}{5+2}\frac{\left(0.029\,\frac{kg}{mol}\right)\left(9.8\,\frac{m}{s^2}\right)}{\left(8.315\,\frac{J}{mol\cdot K}\right)} = -9.8\,\frac{K}{km}$$

This result says that the vertical temperature gradient necessary for dry spontaneous convection is a constant, independent of temperature and pressure. This quantity is known as the **dry adiabatic lapse rate.**

Let's now include the effects of water vapor in the atmosphere, which makes this a multi-phase thermodynamic system. When a rising air mass becomes saturated, the condensing water droplets will release latent heat, thus slowing the adiabatic cooling process. As condensation occurs during this process, the temperature of the air mass will change as a function of water vapor and total pressure. As mentioned above, the condition for convection to occur is that the rising air mass must *remain* warmer than the surrounding air despite the adiabatic cooling of the air mass. We will use the first law, the barometric equation, and the Clausius-Clapeyron relation to determine the temperature gradient necessary for moist convection to occur.

Let's treat the entire rising air mass, including the water vapor and water droplets, as the thermodynamic system. Since all latent heat release remains within the system, there is no net heat exchange between the system and its environment. This is known as a **moist adiabatic process** and thus $dQ = 0$. Since we are concerned about the total internal energy of the air mass and its work on the surrounding environment during condensation processes, we will use enthalpy to examine this process. The thermodynamic identity associated with enthalpy for our moist adiabatic process is given by

$$dH = V\,dP$$

The enthalpy of the system is the sum of the enthalpy of the dry air and the enthalpy of the water substance (both vapor and liquid). The change in the enthalpy of the dry air is

$$dH_{d.a.} = dU + d(PV) = nC_P dT$$

where C_P is the molar specific heat at constant pressure and n is the number of moles of dry air. The dominant contribution to the change in enthalpy of the water substance comes from condensation. Therefore, the change in enthalpy of the water substance is

$$dH_w \approx L\,dn_w$$

where n_w is the number of moles of water vapor pressure. Using these contributions to enthalpy in the thermodynamic identity gives

$$dH_{d.a} + dH_w = V\,dP \Rightarrow nC_P dT + L dn_w = \frac{nRT}{P}dP$$

where, in the last equality, the ideal gas law has been used. Using the barometric equation in the above expression gives

$$nC_P dT + L dn_w = \frac{nRT}{P}\left(-\frac{Mg}{RT}P dz\right) = -nMg\,dz$$

Therefore, our vertical temperature gradient becomes

$$\frac{dT}{dz} = \frac{Mg}{C_P} - \frac{L}{nC_P}\frac{dn_w}{dz}$$

Note that in the case where we have no water vapor ($n_w = 0$), the above relationship simplifies to the adiabatic lapse rate. This expression states that the critical temperature gradient for convection depends on the vertical distribution of water vapor in the atmosphere. As the amount of water vapor increases in the atmosphere, the critical temperature gradient decreases. Thus, when a rising air mass becomes saturated, the air mass becomes even more unstable to convection and tends to rise more quickly, regardless of the initial temperature and pressure.

Now let's assume that the air is always saturated during this process. Because the air and the water vapor are both approximately ideal gases, the ratio n_w/n should be the same as P_v/P, the ratio of the vapor pressure to the total pressure (this also assumes that the water vapor makes up only a small fraction of the air so P is approximately the same as the partial pressure of the dry air). Therefore,

$$\frac{n_w}{n} = \frac{P_v}{P} \Rightarrow n_w = n\frac{P_v}{P}$$

Moreover, notice that n_w depends on the temperature since P_v depends on the temperature through the vapor pressure equation. This implies that dn_w/dz can be written as a function of dT/dz, dP/dz, and $P_v(T)$. To demonstrate this, we differentiate n_w with respect to z to obtain

$$\frac{dn_w}{dz} = \left(\frac{\partial n_w}{\partial T}\right)_P \frac{dT}{dz} + \left(\frac{\partial n_w}{\partial P}\right)_T \frac{dP}{dz} = \frac{n}{P}\left(\frac{\partial P_v}{\partial T}\right)_P \frac{dT}{dz} - \left(\frac{nP_v}{P^2}\right)\frac{dP}{dz}$$

Using the vapor pressure equation and the barometric equation to rewrite the above expression gives

$$\frac{dn_w}{dz} = \frac{n}{P}\left(\frac{\partial P_v}{\partial T}\right)_P \frac{dT}{dz} - \left(\frac{nP_v}{P^2}\right)\frac{dP}{dz} = \frac{n}{P}\left(\frac{LP_v}{RT^2}\right)\frac{dT}{dz} - \left(\frac{nP_v}{P^2}\right)\left(-\frac{Mg}{RT}P\right)$$

Simplifying this expression gives

$$\frac{dn_w}{dz} = \frac{n}{P}\frac{LP_v}{RT^2}\frac{dT}{dz} + \frac{ngMP_v}{PRT}$$

Therefore, our critical temperature gradient for moist convection can be written as

$$\frac{dT}{dz} = \frac{Mg}{C_P} - \frac{L}{nC_P}\frac{dn_w}{dz} = \frac{Mg}{C_P} - \frac{L}{nC_P}\left(\frac{n}{P}\frac{LP_v}{RT^2}\frac{dT}{dz} + \frac{ngMP_v}{PRT}\right)$$

Rearranging gives

$$\left(1 + \frac{P_vL^2}{c_PPRT^2}\right)\frac{dT}{dz} = -\frac{Mg}{c_P}\left(1 + \frac{LP_v}{PRT}\right)$$

Therefore, our critical temperature gradient is given by

$$\Gamma_m \equiv -\frac{dT}{dz} = \left(\frac{Mg}{c_P}\right)\cdot\frac{1 + \frac{LP_v}{PRT}}{1 + \frac{P_vL^2}{c_PPRT^2}}$$

The above expression is called the **moist adiabatic lapse rate** and it is accurate as long as the water vapor and water droplets make up only a small percentage of the mass of the system. The **moist adiabatic lapse rate** is the critical temperature gradient above which saturated air will spontaneously convect. The prefactor is the dry adiabatic lapse rate, while the rest of the expression gives the correction due to heating from the condensing water vapor.

The correction factor can be quite large depending on the conditions of the atmosphere. For instance, the correction factor at 1 bar (i.e. atmospheric pressure) and 0^0C is approximately 0.66, implying that the lapse rate is only 6.5 K/km for saturated air under these conditions. Whereas, the correction factor at 1 bar and 25^0C is approximately 0.41, implying that the lapse rate is 4.0 K/km for saturated air under these conditions. This also shows that the moist adiabatic lapse rate decreases with temperature. In other words, saturated air tends to convect more readily when it's warmer. This can be inferred from the vapor pressure equation. In order for liquid to remain at equilibrium with vapor for high temperatures, the vapor pressure must increase. This can only occur in the atmosphere if the amount of water vapor in the air increases as the temperature increases. This also implies that the rate at which droplets must form (and thus release latent heat) is much greater in warmer areas. This explains why deep moist convection tends to occur preferentially in very warm, moist environments.

7.3 The van der Waals Model

Since the ideal gas model does not include the effect of intermolecular interactions, phase transformations cannot occur for an ideal gas. Therefore, to model phase transformations and to understand phase transformations more deeply, we need to introduce a more suitable mathematical model more suitable for multi-phase systems. The simplest model that grasps some essential features of the liquid-gas phase transformation is the **van der Waals model** of real gases. The van der Waals model (vdW) is an equation of state that modifies the ideal gas law by taking molecular interactions into account in an approximate way.

The van der Waals model is given by

$$\left(P + \frac{aN^2}{V^2} \right)(V - Nb) = NkT$$

As shown above, the van der Waals model makes two modifications to the ideal gas law: adding aN^2/V^2 to the pressure and subtracting Nb from the volume. The first modification accounts for the short-range attractive forces between molecules when they aren't touching. Imagine freezing all the molecules in place so that the only type of energy present is the negative potential energy due to molecular attraction. If we were to double the density of the system, each molecule would then have twice as many neighbors as before, so the potential energy due to all its interactions with neighbors would double. In other words the potential energy associated with a single molecule's interactions with all its neighbors is proportional to the density of particles, N/V. The *total* potential energy associated with all molecules' interactions must then be proportional to $N(N/V) = N^2/V$, since there are N molecules. Thus, we can write the intermolecular potential energy as

$$U_{pot} = -\frac{aN^2}{V}$$

where a is some positive constant of proportionality that depends on the type of molecules. To calculate the pressure from this portion of the internal energy, we recall that $P = -(\partial U/\partial V)_S$. Therefore, the contribution to the pressure from just the potential energy is

$$P_{eff} = P - \left(\frac{\partial U}{\partial V} \right)_S = P + \frac{aN^2}{V^2}$$

The second modification accounts for the minimum volume occupied by a single molecule, when they are "touching". A fluid cannot be compressed all the way down to zero volume, so the van der Waals model limits the volume to a minimum value of Nb, at which the pressure approaches infinity. The constant b then represents the minimum volume occupied by a molecule, when it's "touching" all its neighbors. Therefore, the contribution to the volume is

$$V_{eff} = V - Nb$$

With these modifications, we have the van der Waals model

$$P_{eff}V_{eff} = NkT \Rightarrow P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

While the van der Waals equation has the right properties to account for the qualitative behavior of real fluids, I need to emphasize that it is *not* exact. The van der Waals model neglects a number of effects, most notably the fact that as a gas becomes more dense it can become inhomogeneous on the microscopic scale: Clusters of molecules can begin to form, violating the assumption that the number of neighbors a molecule has will be directly proportional to N/V. Therefore, the van der Waals model should be used only to develop a *qualitative* understanding of the liquid-gas phase transformation.

As mentioned above, the constant a represents the effect of an attractive interaction between the molecules if a is positive (and a repulsion if a is negative) whereas the constant b represents the volume of a single molecule. That is why, for the ideal gas whose molecules are taken to be point-like and non-interacting, both a and b are vanishing, which returns the ideal gas equation of state. The constants a and b will have difference values for different substances, as shown in Figure 7.5. The magnitude of b is roughly the volume of a molecule. The magnitude of a has large variability since it depends on the intermolecular interactions – in other words, some types of molecules attract each other much more strongly than others. In Figure 7.5, note that a is strongest between polar molecules and weakest for inert gases.

Substance	a' $(J \cdot m^3/mol^2)$	b' $(\times 10^{-5} \, m^3/mol)$
Air	.1358	3.64
Carbon Dioxide (CO_2)	.3643	4.27
Nitrogen (N_2)	.1361	3.85
Hydrogen (H_2)	.0247	2.65
Water (H_2O)	.5507	3.04
Ammonia (NH_3)	.4233	3.73
Helium (He)	.00341	2.34
Freon (CCl_2F_2)	1.078	9.98

Figure 7.5 Selected values of *a* and *b* for the van der Waals model for various gases

7.3.1 The Fundamental Surface for the vdW Model

The fundamental surface for the vdW model can be determined by using Gibbs equation in terms of entropy.

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{dU}{T} + \left(\frac{Nk}{V-Nb} - \frac{\frac{aN^2}{V^2}}{T} \right)dV = \frac{NkdV}{V-Nb} + \frac{dU - \frac{aN^2}{V^2}dV}{T}$$

$$= \frac{NkdV}{V-Nb} + \frac{d\left[U + \frac{aN^2}{V^2} \right]}{T}$$

Here T is an integrating factor that makes the last term an exact differential so it must have the form

$$T = F\left(U + \frac{aN^2}{V} \right)$$

In the limit as the intermolecular forces become vanishing, $T \to (2/fNK)U$. This implies that

$$T = \frac{2}{fNK}\left(U + \frac{aN^2}{V} \right)$$

Therefore, the entropy is given by

$$S(U,V) = Nk\left[\ln\left(\frac{V-Nb}{V_0-Nb} \right) + \frac{f}{2}\ln\left(\frac{U + \frac{aN^2}{V}}{U_0 + \frac{aN^2}{V_0}} \right) \right]$$

This can be inverted to give $U(S,V)$.

Since we know the equation of state for the vdW gas, we can write the thermodynamic potentials in terms of measurable variables. The internal energy of the vdW model is given by

$$U(T,V) = \frac{f}{2}NkT - \frac{N^2a}{V}$$

The enthalpy for the vdW gas is given by

$$H(T,V) = U(T,V) + P(T,V)V = \frac{f}{2}NkT - \frac{N^2a}{V} + P(T,V)V = -\frac{2aN^2}{V} + \frac{f}{2}NkT + \frac{NkTV}{V - Nb}$$

We will examine the Helmholtz free energy and the Gibbs free energy in the next section.

7.3.2 Thermodynamic processes for the vdW model

We can also examine the basic quasistatic thermodynamic processes for a vdW gas. For isochoric processes, the first law states that

$$\Delta U = Q = C_V \Delta T$$

The heat capacity at constant volume is given by

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V = \frac{f}{2}Nk$$

Therefore, the change in internal energy is the same as in an ideal gas

$$\Delta U = \frac{f}{2}Nk\Delta T = \frac{f}{2}Nk(T_2 - T_1)$$

For isobaric processes, the work done is given by

$$W = -\int_{V_1}^{V_2} P\, dV = -P(V_2 - V_1)$$

The heat entering the system is given by

$$Q = C_P \Delta T = C_P(T_2 - T_1)$$

To complete this, we need to determine the heat capacity at constant pressure. Recall that the specific heats of any thermodynamic system can be related as

$$C_P = C_V + T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

It can be shown that the heat capacity at constant pressure for the vdW gas is given by

$$C_P = Nk \left[\frac{f}{2} + \frac{P + \frac{aN^2}{V^2}}{P - \frac{aN^2}{V^2} + \frac{2abN^3}{V^3}} \right]$$

For an isothermal process, the change in potential energy is given by

$$U = \frac{f}{2} NkT - \frac{aN^2}{V} \Rightarrow \Delta U = N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

The work done is given by

$$W = - \int_{V_1}^{V_2} P(T,V) dV = - \int_{V_1}^{V_2} \left(\frac{NkT}{V - Nb} - \frac{N^2 a}{V^2} \right) dV = -NkT \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right) + N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

The heat added or absorbed is given by

$$Q = \Delta U - W = NkT \ln \left(\frac{V_2 - Nb}{V_1 - Nb} \right)$$

For an adiabatic process, we can write the adiabatic equation of state as

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb)^\gamma = const.$$

The change in internal energy is given by

$$\Delta U = \frac{f}{2} Nk(T_2 - T_1) + N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

According to the first law, note that $W = \Delta U$

7.4 Liquid-Gas Phase Transition
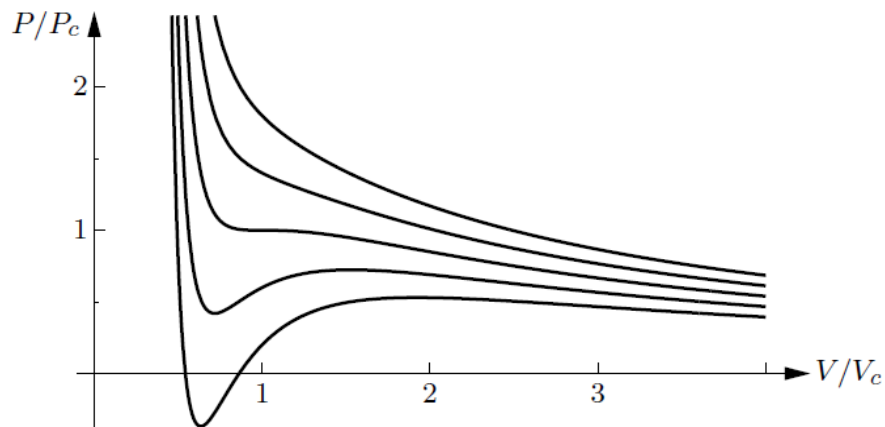
Figure 7.6 Isotherms for a van der Waals fluid. From bottom to top, the lines are 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c, the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point.

We are now going to use the vdW model to determine the qualitative properties of the liquid-gas phase transition. We can investigate the consequences of the van der Waals model by plotting the predicted pressure as a function of volume for a variety of different temperatures, as shown in Figure 7.6. For $V \gg Nb$, the isotherms are similar to those of an ideal gas. At sufficiently high temperatures, reducing the volume causes the pressure to rise smoothly, eventually approaching infinity as the volume goes to Nb (similar to an ideal gas). At lower temperatures, however, the behavior is much more complex. As V decreases, the isotherms admit an inflection point at positive volume and pressure. As a result, the van der Waals isotherms seem to imply that for some states, fluid compression can cause its pressure to decrease. This is unphysical behavior and signals a potential breakdown of the equation of state. However, a careful analysis shows that the van der Waals model doesn't produce this behavior either. We will first analyze this through Gibbs free energy and then through Helmholtz free energy.

7.4.1 Gibbs free energy analysis

At a given temperature and pressure, the true equilibrium state of a system is determined by its Gibbs free energy. To calculate G for a van der Waals fluid, let's start with the Pfaffian of G (written in terms of the number of molecules)

$$dG = -SdT + VdP + \mu dN$$

For a fixed amount of material at a given temperature, this equation reduces to

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}$$

The right hand side can be computed directly from the van der Waals equation of state, yielding

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

\noindent Integrating the above equation gives

$$G(T,V) = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + c(T)$$

where the integration constant $c(T)$ can be different temperatures but is unimportant for our purposes. The equation allows us to plot the Gibbs free energy for any fixed T.
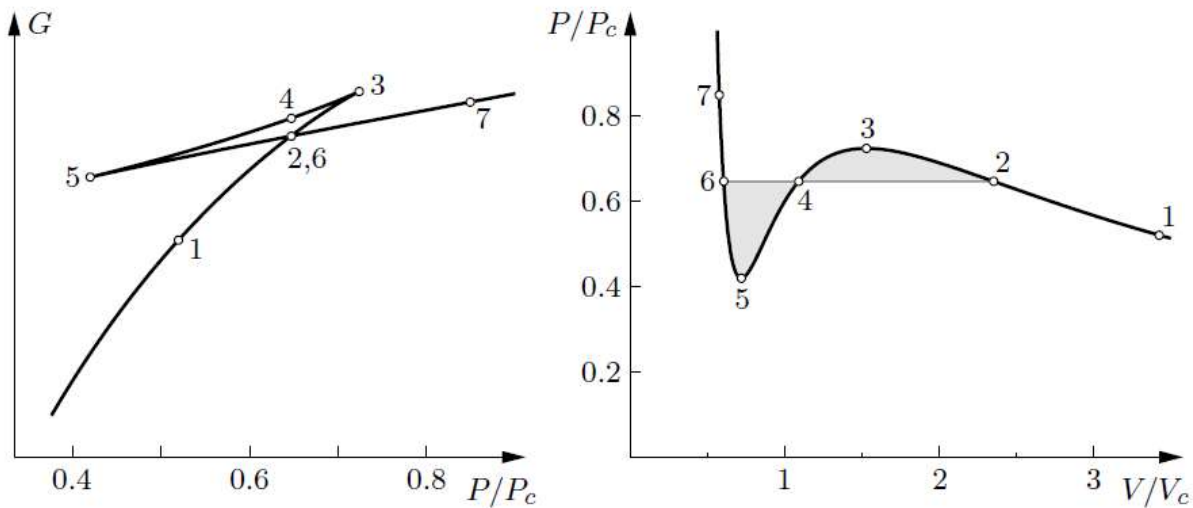
Figure 7.7 Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

Instead of plotting G as a function of volume, it's more useful to plot G vertically and P horizontally, calculating each as a function of the parameter V. Figure 7.7 shows an example, for the temperature whose isotherm is shown alongside. Although the van der Waals equation associated some pressures with more than one volume, the thermodynamically stable state is that with the lowest Gibbs free energy. Thus, the triangular loop in the graph of G (points 2-3-4-5-6) corresponds to unstable states. As the pressure is gradually increased, the system will go straight from point 2 to point 6, with an abrupt decrease in volume, i.e. a phase transformation. At point 2, we should call this fluid a gas because its volume decreases rapidly with increasing pressure. At point 6, we should call the fluid a liquid because its volume decreases only slightly under a large increase in pressure. At intermediate volumes between these points, the thermodynamically stable state is actually a combination of gas and liquid, still at the transition pressure, as indicated by the straight horizontal line on the PV diagram. The curved portion of the isotherm that is cut

183

off by this straight line correctly indicates what the allowed states *would* be if the fluid were homogeneous, but these homogeneous states are unstable since there is always another state (gas or liquid) at the same pressure with a lower Gibbs free energy.
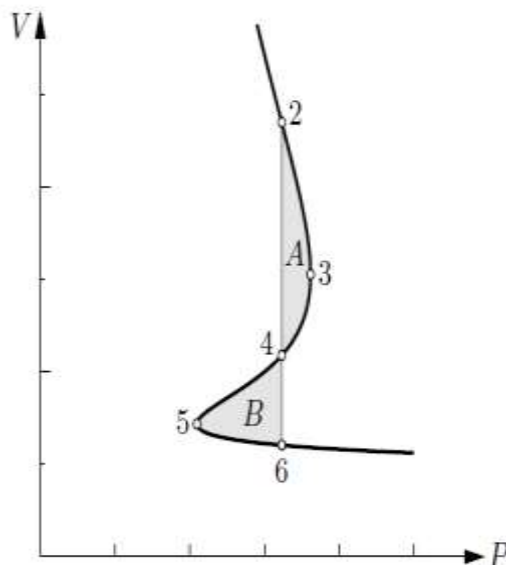
Figure 7.8 The same isotherm as in Figure 7.7, plotted sideways. Regions A and B have equal areas.

The pressure at the phase transformation can be read straight off the *PV* diagram without plotting *G* at all. To derive this method, note that the net change in *G* as we go around the triangular loop (2-3-4-5-6) is zero:

$$\oint dG = \oint \left(\frac{\partial G}{\partial P}\right)_T dP = \oint V \, dP = 0$$

Written in this last form, the integral can be computed from the *PV* diagram (see Figure 7.8). The integral from point 2 to point 3 gives the entire area under this segment, but the integral from point 3 to point 4 cancels out all but the shaded region *A*. The integral from 4 to 5 gives minus the area under that segment, but then the integral from 5 to 6 adds back all but the shaded region *B*. Thus the entire integral equals the area of *A* minus the area of *B*, and if this is equal to zero, we conclude that the two shaded regions must have equal areas. Drawing a straight line so as to enclose equal areas in this way is called the **Maxwell construction**.
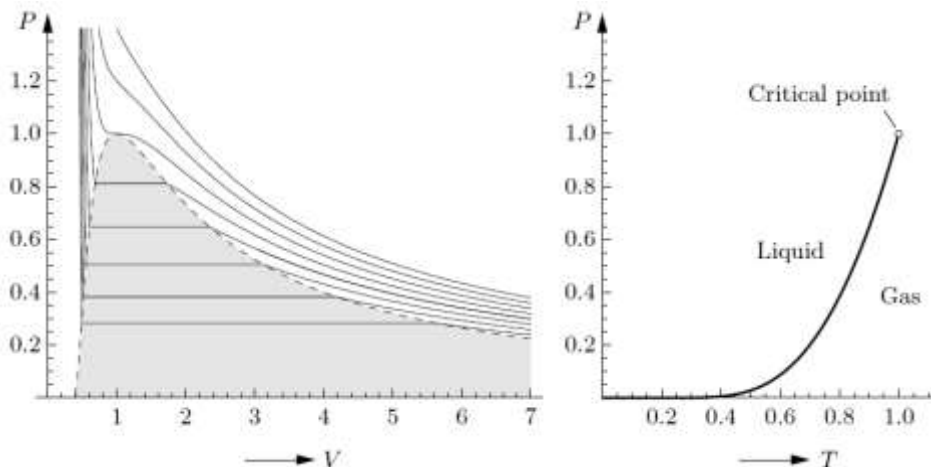
Figure 7.9 Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1. in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.

Repeating the Maxwell construction for a variety of temperature yields the results shown in Figure 7.9. For each temperature there is a well-defined pressure (the vapor pressure) at which the liquid-gas phase transformation takes place. Plotting this pressure vs. temperature gives us a prediction for the entire liquid-gas phase boundary. Meanwhile, the straight segments of the isotherms on the *PV* diagram fill a region in which the stable state is a combination of gas and liquid, indicated by the shaded area. Note that the high-temperature isotherms rise monotonically as *V* decreases. For these temperatures, there is no abrupt transition from low-density states to high-density states (i.e. no phase transformation). Therefore, the phase boundary disappears above a certain temperature called the **critical temperature** T_c. The vapor pressure just at T_c is called the **critical pressure** P_c, while the corresponding volume is called the **critical volume**, V_c. These values define the **critical point**, where the properties of the liquid and gas become identical.
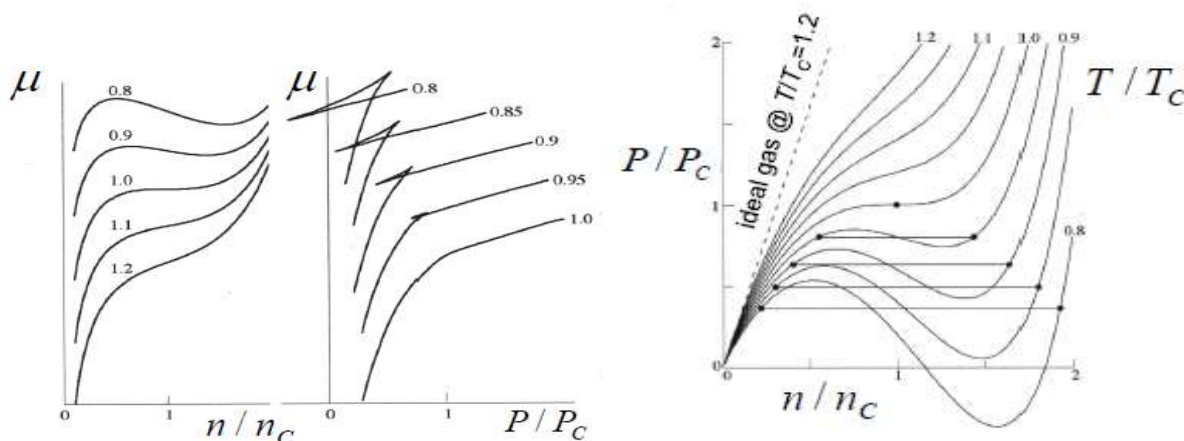
Figure 7.10 Chemical potential as a function of pressure and moles for a van der Waals fluid for various isotherms. From top to bottom, the lines are 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c. The corresponding isotherms are shown at right.

185

Figure 7.10 shows the same essential result in terms of the chemical potential. For isotherms below the critical temperature, there are three values of n with the same μ. The outer two values of n correspond to two stable phases which are in equilibrium with each other. The "kink" on the $G(V)$ curve is a signature of the 1$^{\text{st}}$ order transition. When we move along the gas-liquid coexistence curve towards the critical point, the transition becomes less and less abrupt, and at the critical point, the abruptness disappears.

Based on Figure 7.9 and 7.10, the critical point is the inflection point on the original van der Waals isotherms (before the Maxwell construction). Therefore, to determine the critical point on the van der Waals isotherms, we set

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c}$$

and solve the set of three equations (the two above and the equation of state) for the pressure, volume, and temperature. It can be shown that the critical values are functions of a and b:

$$V_c = 3b, \;\; P_c = \frac{a}{27b^2}, \;\; kT_c = \frac{8a}{27b}$$

We see that a model as simple as the van der Waals equation predicts *all* of the important qualitative properties of real fluids: the liquid-gas phase transformation, the general shape of the phase boundary curve, and even the critical point. However, the model fails to produce *quantitative* predictions. For example, the experimental phase boundary for H_2O falls more steeply from the critical point than does the predicted boundary shown in Figure 7.9. At $T/T_c = 0.8$, the measured vapor pressure is only about $0.2P_c$, instead of $0.4P_c$ as predicted. More accurate models of the behavior of dense fluids are beyond the scope of these notes.

7.4.2 Helmholtz Free Energy Analysis

The phase transformation in the van der Waals model is easier to analyze by minimizing $F(V)$ rather than $G(P)$. Figure 7.11 shows an isotherm below the critical point. At $T < T_C$, there is a region on the $F(V)$ curve becomes concave and thus a common tangent line can be drawn to connect V_1 and V_2. Since the common tangent line lies below $F(V)$, molecules can minimize their free energy by refusing to be in a single homogeneous phase in the region between V_1 and V_2 and thus we have **two coexisting phases.** Let's show how this can be done.
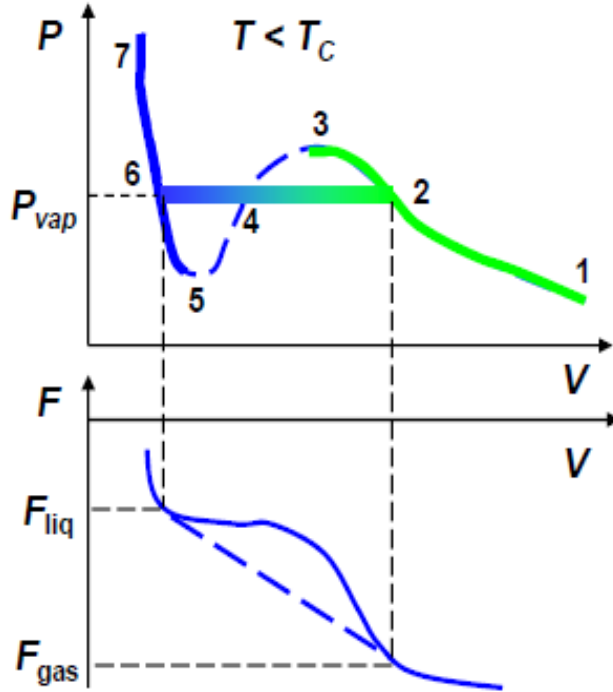
Figure 7.11 A schematic of an isotherm for a van der Waals fluid below the critical temperature. The isotherm is plotted in terms of Helmholtz free energy below it.

Now suppose the system consists of a combination of two different states (e.g. liquid and gas). Let x be the fraction (by mass) of liquid, so the fraction of gas is $1 - x$. The total volume of the system is then

$$V = xV_{liq} + (1 - x)V_{gas} = V_{gas} - x(V_{gas} - V_{liq}) \Rightarrow x = \frac{V - V_{gas}}{V_{liq} - V_{gas}}$$

By the same reasoning (since they are both extensive variables), the total Helmholtz free energy is

$$F = xF_{liq} + (1 - x)F_{gas} = F_{liq}\left(\frac{V - V_{gas}}{V_{liq} - V_{gas}}\right) + F_{gas}\left(\frac{V_{liq} - V}{V_{liq} - V_{gas}}\right)$$

$$= F_{gas} - \frac{(V_{gas} - V)}{(V_{gas} - V_{liq})}(F_{gas} - F_{liq})$$

This equation for $F(V)$ describes a straight line going through the points (V_{liq}, F_{liq}) and (V_{gas}, F_{gas}). It is drawn as a dashed line in Figure 7.11. Notice that this straight line lies *below* the original curve representing the free energy of a homogeneous state of uniform density. Since a system at constant T and V tends to minimize its free energy, the stable states at volume V_1 and V_2 are those represented by the dashed line, not the solid curve. Notice also that at the points

187

where the line meets the curve at each end, it is tangent to the curve, indicating that this is the lowest possible line that can be drawn between any two points on the curve, lying entirely below it. In fact, had we not known the transition volumes V_1 and V_2, we could have found them by drawing the lowest possible such straight line and then looking at where it meets the curve at a tangent. This process is another way of doing the Maxwell construction.

To see this in another way, recall that the thermodynamic pressure can be written based on the partial derivative of the Helmholtz free energy:

$$dF = -SdT - PdV \Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Since the tangent line maintains the same slope between V_1 and V_2, the pressure remains constant between V_1 and V_2. In other words, the line connecting points on the PV plot is horizontal and the two coexisting phases are in mechanical equilibrium. For each temperature below T_C, the phase transformation occurs at a well-defined pressure called the **vapor pressure.**

In Figure 7.11, the two stable branches 1-2-3 and 5-6-7 correspond to different phases. Along 1-2-3, volume is large , pressure is small, and density is small – gas phase. Along 5-6-7, volume is small, pressure is large, and density is large – liquid phase. Between the branches, we have the gas-liquid phase transformation.

7.5 Nucleation

So far, we have ignored the *boundary* between two phases, as if each molecule were unequivocally part of one phase or the other. In fact, the boundary is a kind of transition zone where molecules are in an environment that differs from both phases. Since the boundary zone is only a few molecules thick, its contribution to the total free energy of a system is very often negligible. One important exception, however, is the first tiny droplets that form as a material begins to undergo a phase transformation. The formation of these initial droplets is called **nucleation**. In this section, we will consider the nucleation of water droplets in a cloud.

The surface forming the boundary between any two given phases generally has a fixed thickness, regardless of its area. The additional Gibbs free energy of this surface is therefore directly proportion to its area. The constant of proportionality is called the **surface tension** σ:

$$\sigma \equiv \frac{G_{boundary}}{A}$$

If you have liquid in equilibrium with its vapor and you wish to stretch it into a shape that has the same volume but more surface area, then σ is the minimum work you must perform, per unit of additional area, at fixed temperature and pressure. For water at $20°C$, $\sigma = 0.073\ J/m^2$.

Let's consider a spherical droplet of water containing N_l molecules, surrounded by $N - N_l$ molecules of water vapor. For any pure system, we can write the Gibbs free energy as $G = \mu N$. For a liquid droplet surrounded by vapor, the total Gibbs free energy would be simply the sum of contributions from the two subsystems plus the contribution from the droplet's surface:

$$G = N_l \mu_l + N_v \mu_v + A\sigma = N_l \mu_l + (N - N_l)\mu_v + A\sigma = N\mu_v + N_l(\mu_l - \mu_v) + A\sigma$$

where the subscript l is for liquid and v is for vapor. If V_l is the volume per molecule in the liquid, then N_l is the ratio of the total volume of the liquid to V_l. Assuming a spherical droplet, we therefore have

$$G = N\mu_v + \frac{4\pi r^3}{3V_l}(\mu_l - \mu_v) + 4\pi r^2 \sigma$$
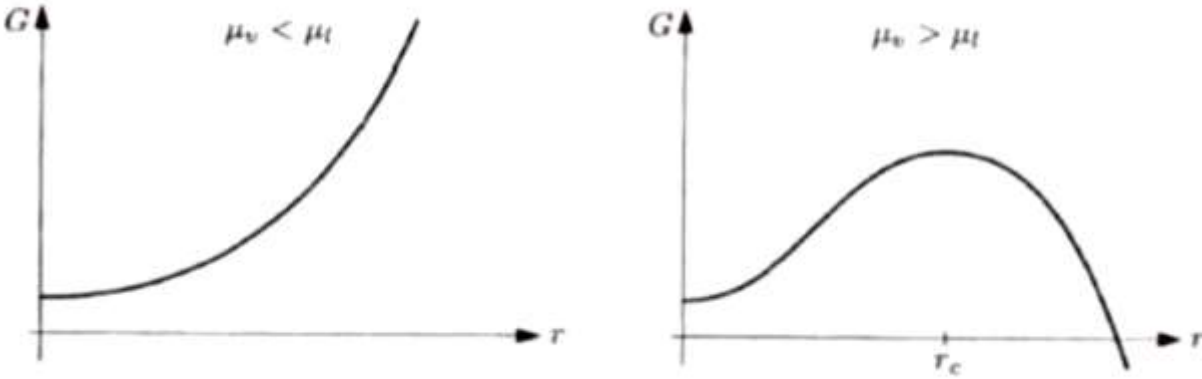
Figure 7.12 Qualitative graph of G vs. r for both signs of $\mu_v - \mu_l$

We note that the Gibbs free energy is a function of radius and surface tension. The r dependence of G comes from the second and third terms in the preceding expression. The third term is always positive and is quadratic in r, so its graph is an upward-opening parabola, as shown in Figure 7.12. The second term is cubic in r, but can be positive or negative depending on which is larger, μ_l or μ_r. If $\mu_l > \mu_v$, indicating that molecules would tend to diffuse from the liquid to the vapor, then this term is positive. This would indicate that the only equilibrium point is the minimum at $r = 0$, so the tendency of G to decrease will cause any water droplet to evaporate and disappear. On the other hand, if $\mu_v > \mu_l$, then the cubic term is negative and thus,

there exist a nontrivial equilibrium radius r_c, where G reaches a maximum. However, this is an unstable equilibrium since droplets smaller than r_c will evaporate, while droplets larger than r_c will grow until the vapor becomes depleted of water molecules causing $\mu_v \leq \mu_l$. To determine the critical radius, we set the derivative of G equal to zero

$$0 = \left(\frac{dG}{dr}\right)_{r_c} = -\frac{4\pi r_c^2}{V_l}(\mu_v - \mu_l) + 8\pi r_c \sigma$$

Solving for r_c gives

$$r_c = \frac{2\sigma v_l}{\mu_v - \mu_l}$$

Now the chemical potential of the vapor can be written in terms of its partial pressure

$$\mu_v = \mu_v(0) + kT \ln\left(\frac{P}{P_0}\right)$$

where the subscript refers to any convenient reference pressure. If we take the reference pressure to be the nominal vapor pressure, that is, the pressure of vapor that would be in equilibrium with a flat surface of the liquid, then P/P_0 is just the **relative humidity** (let's call it RH) and $\mu_v(0) = \mu_l$. The difference $\mu_v - \mu_l$ can therefore be written as $kT \ln(RH)$, and our expression for the critical radius becomes

$$r_c = \frac{2\sigma V_l}{kT \ln(RH)} \Rightarrow RH = \exp\left[\left(\frac{2\sigma V_l}{kTr_c}\right)\right] = \exp\left[\left(\frac{2\sigma v_l}{RTr_c}\right)\right]$$

where v_l is the molar volume of liquid. This result is known as the **Kelvin equation**. For water at 20°C, the Kelvin equation predicts that $r_c = (1.08 \, nm) \ln(RH)$. The critical radius goes to zero as the relative humidity goes to infinity and goes to infinity as the relative humidity goes to 100%. We know from experience that the relative humidity in our atmosphere is never much greater than 100%; therefore, according to this analysis, droplets smaller than about 10 nm in radius should never be stable. We are forced to conclude that cloud droplets in our atmosphere must nucleate through some other process. In fact, cloud droplets form around nuclei of dust particles and other foreign material (called **aerosols**) when the relative humidity is close to 100%. A detailed analysis on the effects of aerosols on nucleation is beyond the scope of these notes.

7.6 Summary of Classical Thermodynamics

Classical thermodynamics is a completely self-contained, phenomenological theory of matter. It is concerned with the properties of a macroscopic system (a system that is extremely large on the molecular scale and consisting of about 10^{24} molecules in equilibrium with the environment). Matter in equilibrium is defined by its equilibrium macrostate, which is a set of variables that adequately describe all the measurable properties of the system. These "macroscopic" or "thermodynamic" variables need not be the mechanical variables of the system but they are, eventually, related to them. Equilibrium macrostates do not change significantly with time.

Thermodynamics is also concerned with processes that take a macroscopic system from some initial equilibrium state to a final equilibrium state, but generally it has little to say about the system during the process itself, unless the process happens to take place very "slowly" compared to the characteristic relaxation time scale of the system. Transformations between equilibrium states come about by relaxing one or more external constraints, thereby letting the system evolve and achieve a new equilibrium state. If the constraints are relaxed slowly, in the sense mentioned, then the system effectively stays in equilibrium at all times and the process is said to be quasi-static. On the other hand, if the constraints are relaxed suddenly, so that the transformation occurs rapidly compared with the relaxation time of the system, the system is out of equilibrium during the transformation process and the process is not quasi-static. In this case, while thermodynamics is unable to describe the process itself, it is able to give us some general conditions under which one equilibrium state may evolve into another. It is based upon three fundamental laws, which we briefly review below.

1. **Zeroth Law:** The law introduces a new variable called the **temperature**. It says that there exists a variable of the macroscopic state called the temperature, which determines thermal equilibrium between two systems. Two thermodynamics systems having the same temperature will not exchange energy by thermal interactions on the average if their temperatures are the same.

2. **First Law**: The law introduces a new variable called the **internal energy**. It says that there exists a function of state called the internal energy and asserts that the total energy is conserved:
$$dU = \delta Q + \delta W$$
where δQ is the heat exchanged between the system and its environment (via temperature differences), and δW is the work done by (on) the system on (by) the environment. Neither δQ nor δW are "exact differentials", which means that their integrals depend on the precise process taking the system from the initial to the final state. However, U being a function of state, dU is indeed an exact differential (its integral depends only on the

initial and final states of the process. The experimental justification for the 1st law is Joule's experiment which demonstrates the equivalence between heat and energy.

3. **Second Law:** This law introduces a new variable called **entropy**, defined such that the change in entropy from some initial state to some final state is given by

$$\Delta S = S_f - S_i = \int\limits_{i,q.s.}^{f} \frac{\delta Q}{T}$$

The second law states that a given thermodynamic process can occur if and only if $\Delta S \geq 0$ *for the corresponding closed or isolated system.* It can be shown that the entropy is a function of state and dS is an exact differential. A reversible process is one in which $\Delta S = 0$; if $\Delta S > 0$, the process is irreversible. A reversible process is quasi-static, but the opposite is not necessarily true. The above expression gives only the change in entropy during a reversible process; therefore, the second law does not serve as a complete definition of entropy. It gives only changes in entropy between initial and final states. The third law completes the thermodynamic definition of entropy by stating its canonical value at a given temperature, which will be derived next chapter.

We will now be interested in the molecular foundations of thermodynamics. Specifically, we will ask ourselves the following question: if mechanics (classical or quantum) provides the fundamental description of the dynamics of particles, atoms and molecules, and if macroscopic systems are indeed built up of these particles, then is it possible to recover a description of macroscopic systems starting with the microscopic dynamics? We want to obtain the macroscopic dynamics from the microscopic dynamics. With the ensuing theory we will be able to analyze the natural fluctuations about equilibrium and, putting it side by side with thermodynamics, we will have a comprehensive mathematical theory that is capable of describing the stability or instability of macroscopic systems.

Chapter 8: Introduction to Statistical Mechanics

In this chapter, we begin our treatment of the molecular foundations of thermodynamics. As mentioned in the previous chapter, the goal of statistical mechanics is to obtain the macroscopic dynamics of a given thermodynamics from the microscopic dynamics. In this chapter, we will introduce the mathematical framework and the essential methodology to address this goal.

8.1 The Fundamental Need for a Statistical Approach

Why do we need something as limited as classical thermodynamics when we have at our disposal all the tools for a complete mechanical description of any system? We can answer this question by asking precisely what such a detailed description would entail.

First, we need to know the initial state of the system. If we are working within classical mechanics this means that we must know the initial positions and momentum vectors of each particle within the system. This "state" would be defined by a set of variables of the form: $\{S\} = \{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N\}$, where N is the number of particles, all obtained (experimentally) at the initial time, say $t = 0$. One can easily count the number of variables in this set: there are $6N$ of them, three positions and three momenta for each particle. Now consider that a mole of any material would contain 6.023×10^{23} molecules, so we would need to measure roughly 3.6×10^{24} variables to determine the initial classical state. To know the quantum state, on the other hand, we would need to know the Schrodinger wave function at some initial time t_i, which involves f quantum numbers, where f is the number of degrees of the system.

Second, we would need to know the detailed interactions between all the particles of the system. Thus, for a system of N particles, we should know all the interaction potentials of U_{ij}. There are $N(N-1)/2$ distinct pairs of N particles, so there are approximately 10^{48} interaction potentials to be determined for every mole of any material. Lastly we need to solve the equations of motion (Newton's equations in a classical treatment or Schrodinger's equation in a quantum), subject to satisfactory boundary conditions. These are generally f coupled equations, because of the interactions between the particles.

It should need no convincing that all three steps in the list above are impossible to carry out in practice. It is impossible to know the precise initial state, very difficult to model all the

intermolecular interactions and again practically impossible to solve approximately 10^{24} coupled equations even with our fastest computers. However, let us consider what such a description would give us if it were possible: in principle it would predict the precise trajectories of each particle in the system, something that we could not hope to measure in the laboratory anyway. Happily, therefore, a precise mechanical or quantum mechanical description is too detailed to be of any practical use.

Nonetheless, we can measure certain properties of a macroscopic system such as its energy, temperature, pressure, volume, etc. This is a relatively small set compared with the huge set of variables required to measure the microscopic state of the system, indeed it is only a small part of the total detailed information that is, in principle, available. We must keep in mind that the choice of this small subset of thermodynamic variables depends on the nature of the system and the kind of experiments being performed. We shall call the variables that are measured and controlled in the laboratory the **macroscopic variables**.

We would like to give the macroscopic variables some mechanical meaning, however. We would also be interested in attempting a more detailed description of macroscopic systems than is afforded by thermodynamics, though not as detailed as a purely mechanical treatment would afford. This is the objective of statistical mechanics, whose goal is to obtain all the equilibrium properties of macroscopic systems by applying the laws of mechanics (thus "deriving" thermodynamics from more fundamental principles and giving mechanical meaning to the thermodynamic variables). It does so by combining mechanics with general statistical principles. Mechanics provides the general physical framework, such as the laws of conservation, and statistics replaces the rigorous detail required by pure mechanics by general, reasonable, statistical assumptions whose validity can only be measured by experiment.

In this chapter, we develop the statistical tools necessary to understand statistical mechanics. We introduce the basic concepts of probability and apply them to simple physical systems and to everyday life. We discuss the universal nature of the central limit theorem and the Gaussian distribution for the sum of a large number of random variables.

8.2 The Meaning of Probability

Suppose that there is an operation or a process that has several distinct possible outcomes. The process might be the flip of a coin or the roll of a six-sided die. We call each flip a **trial**. The list of all the possible events or outcomes is called the **sample space**. We assume that the events are **mutually exclusive**, that is, the occurrence of one event implies that the others cannot happen at the same time. We let n represent the number of events, and label the events by the index i which varies from 1 to n. For now we assume that the sample space is finite and

discrete. For example, the flip of a coin results in one of two events, which we refer to as heads and tails and the roll of a die yields one of six possible events.

For each event i, we assign a probability $P(i)$ that satisfies the following conditions:

$$P(i) \geq 0, \quad \sum_i P(i) = 1$$

For a discrete and finite sample space, $P(i) = 0$ means that the event *cannot* occur, and $P(i) = 1$ means that the event *must* occur. The second condition (known as the normalization condition) says that the sum of the probabilities of all possible mutually exclusive outcomes is 1. The rules of probability will be summarized in the following section, but these rules must be supplemented by an *interpretation* of the term probability. As we will see, there are many different interpretations of probability because any interpretation that satisfies the rules of probability may be regarded as a kind of probability.

A common interpretation of probability is based on *symmetry*. Suppose that we have a two-sided coin that shows heads and tails. There are two possible mutually exclusive outcomes and if the coin is fair, each outcome is equally likely. If a die with six distinct faces is perfect, we can use symmetry arguments to argue that each outcome should be counted equally and $P(i) = 1/6$ for each of the six faces. For an actual die, we can estimate the probability of an outcome *a posteriori*, that is, by the observation of the outcome of many throws. As we will see, other kinds of information in addition to symmetry arguments can be used to estimate probabilities.

How can we assign probabilities to the various events? If event E_1 is more probable than event E_2, we mean that E_1 is more likely to occur than E_2. This statement of our intuitive understanding of probability illustrates that probability is a way of classifying the plausibility of events under conditions of uncertainty. Probability is related to our degree of belief in the occurrence of an event.

The definition of probability is not bound to a single evaluation rule (as mentioned previously) and there are many ways to obtain $P(E_i)$. For example, we could use symmetry considerations as we have done, past frequencies, simulations, or theoretical calculations. Probability assessments depend on who does the evaluation and the status of the information the evaluator has at the moment of the assessment. In other words, we always evaluate the conditional probability – that is the probability of an event E given the information I. Consequently, several people can have simultaneously different degrees of belief about the same event.

If rational people have access to the same information, they should come to the same conclusion about the probability of an event. The idea of a *coherent bet* forces us to make

probability assessments that correspond to our belief in the occurrence of an event. If we consider an event to be 50% probable, then we should be ready to place an even bet on the occurrence of the event or on its opposite. However, if someone wishes to place the bet in one direction but not in the other, it means that this person thinks that the preferred event is more probable than the other. In this case the 50% probability assessment is incoherent, and this person's wish does not correspond to his or her belief.

A coherent bet has to be considered virtual. For example, a person might judge an event to be 99.9999% probable, but nevertheless refuse to bet $999999 against $1, if $999999 is much more than the person's resources. Nevertheless, the person might be convinced that this bet would be fair if he/she had an infinite budget. Probability assessments should be kept separate from decision issues. Decisions depend not only on the probability of the event, but also on the subjective importance of a given amount of money.

Our discussion of probability as the degree of belief that an event will occur shows the inadequacy of the frequency definition of probability, which *defines* probability as the ratio of the number of desired outcomes to the total number of possible outcomes. This definition is inadequate because we would have to specify that each outcome has equal probability. Thus we would have to use the term probability in its own definition. If we do an experiment to measure the frequencies of various outcomes, then we need to make an additional assumption that the measured frequencies will be the same in the future as they were in the past. Also we have to make a large number of measurements to ensure accuracy, and we have no way of knowing a priori how many measurements are sufficient. Thus, the definition of probability as a frequency really turns out to be a method for estimating probabilities with some hidden assumptions.

Our definition of probability as a measure of the degree of belief in the occurrence of an outcome implies that probability depends on our prior knowledge, because belief depends on prior knowledge. For example, if we toss a coin and obtain 100 tails in a row, we might use this knowledge as evidence that the coin or toss is biased, and thus estimate that the probability of throwing another tail is very high. However, if a careful physical analysis shows that there is no bias, then we would stick to our estimate of 1/2. The probability assessment depends on what knowledge we bring to the problem. If we have no knowledge other than the possible outcomes, then the best estimate is to assume equal probability for all events. However, this assumption is not a definition, but an example of belief.

8.2.1 Estimation of Probability

We know that we can estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent events. Intuitively we believe that if we

perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called the **law of large numbers**. As an example, suppose that we flip a single coin M times and count the number of heads. Our result for the number of heads is shown in Figure 8.1. We see that the fraction of heads approaches 1/2 as the number of measurements becomes larger.

tosses	heads	fraction of heads
10	4	0.4
50	29	0.58
100	49	0.49
200	101	0.505
500	235	0.470
1,000	518	0.518
10,000	4997	0.4997
100,000	50021	0.50021
500,000	249946	0.49999
1,000,000	500416	0.50042

Figure 8.1 The number and fraction of heads in M tosses of a coin, evaluated by numerical simulation

Another way of estimating the probability is to perform a single measurement on many copies or replicas of the system of interest. For example, instead of flipping a single coin 100 times in succession, we collect 100 coins and flip all of them at the same time. The fraction of coins that show heads is an estimate of the probability of that event. The collection of identically prepared systems is called an **ensemble**, and the probability of occurrence of a single event is estimated with respect to this ensemble. The ensemble consists of a large number M of identical systems, that is, systems that satisfy the same known conditions. If the system of interest is not changing in time, it is reasonable to assume that an estimate of the probability by either a series of measurements on a single system at different times or similar measurements on many identical systems at the same time would give consistent results.

Note that we have *estimated* various probabilities by a frequency, but have not *defined* probability in terms of a frequency. Past frequency is experimental data and since it is in the past, this data happened with certainty so the concept of probability no longer applies. Probability is how much we believe that an event will occur taking into account all available information including past frequencies. Because probability quantifies the degree of belief at a given time, it is not directly measurable. If we make further measurements, they can only influence future assessments of the probability.

197

8.2.2 Information and Uncertainty

Consider two experiments that each have two outcomes, E_1 and E_2 with probabilities P_1 and P_2. For example, the experiments could correspond to the toss of a coin. In the first experiment, the coin has probabilities $P_1 = P_2 = 1/2$, and in the second experiment (a bent coin) $P_1 = 1/5$ and $P_2 = 4/5$. Intuitively, we would say that the result of the first experiment is more uncertain than the result of the second experiment.

Next, consider two additional experiments. In the third experiment there are four outcomes with $P_1 = P_2 = P_3 = P_4 = 1/4$, and in the fourth experiment there are six outcomes with $P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = 1/6$. The fourth experiment is the most uncertain because there are more equally likely outcomes and the second experiment is the least uncertain.

We will not introduce a mathematical measure that is consistent with our intuitive sense of uncertainty. Let us define the uncertainty function $S(P_1, P_2, \dots, P_i, \dots)$, where P_i is the probability of event i. We first consider the case where all the probabilities P_i are equal. Then $P_1 = P_2 = \dots = P_i = 1/\Omega$, where Ω is the total number of outcomes, which implies that $S(\Omega)$.

Based on our intuition, $S(\Omega)$ has to satisfy some simple conditions. For only one outcome, $\Omega = 1$ and there is no uncertainty. Hence, we must have that
$$S(\Omega = 1) = 0$$
We also have that
$$S(\Omega_1) > S(\Omega_2) \; if \; \Omega_1 > \Omega_2$$
which means that $S(\Omega)$ is an increasing function of Ω.

We next consider the form of S for multiple events. For example, suppose that we throw a die with Ω_1 outcomes and flip a coin with Ω_2 equally probable outcomes. The total number of outcomes is $\Omega = \Omega_1 \Omega_2$. If the result of the die is known, the uncertain associated with the die is reduced to zero, but there still is uncertainty associated with the toss of the coin. Similarly, we can reduce the uncertainty in the reverse order, but the total uncertainty is still nonzero. These considerations suggest that

$$S(\Omega_1 \Omega_2) = S(\Omega_1) + S(\Omega_2)$$

It turns out that there is an unique functional form that satisfies the three aforementioned conditions. We can find this form by writing the above expression as

$$S(xy) = S(x) + S(y)$$

and taking the variables x and y to be continuous. Now, we take the partial derivative of $S(xy)$ with respect to x and then with respect to y. Letting $z = xy$, we obtain

$$\frac{\partial S(z)}{\partial x} = \frac{dS(z)}{dz}\frac{\partial z}{\partial x} = y\frac{dS(z)}{dz}$$
$$\frac{\partial S(z)}{\partial y} = \frac{dS(z)}{dz}\frac{\partial z}{\partial y} = x\frac{dS(z)}{dz}$$

However, we also know that

$$\frac{\partial S(z)}{\partial x} = \frac{dS(x)}{dx}, \qquad \frac{\partial S(z)}{\partial y} = \frac{dS(x)}{dy}$$

Comparing these expressions gives

$$\frac{dS}{dx} = y\frac{dS}{dz}, \qquad \frac{dS}{dy} = x\frac{dS}{dz} \Rightarrow x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy}$$

Because x and y are independent variables, we must have

$$x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy} = A \Rightarrow S(x) = A\ln x + B$$

The integration constant B must be zero so that $S(1) = 0$. The constant A is arbitrary so we choose $A = 1$. Hence for equal probabilities, we have that $S(\Omega) = \ln \Omega$. What about the case where the probability for the various events are unequal? We will not derive the result here, but only state that the general form of the uncertainty S is

$$S = -\sum_i P_i \ln P_i$$

We have shown that, if the P_i are known, then the uncertainty or missing information S can be calculated. Usually the problem is the other way around, and we want to determine the probabilities. Suppose we flip a perfect coin for which there are two possibilities. We expect that $P_1(heads) = P_2(tails) = 1/2$. That is, we would not assign a different probability to each outcome unless we had information to justify it. Intuitively, we have adopted the principle of *least bias* or *maximum uncertainty*. Let's reconsider the toss of a coin. In this case S is given by

$$S = -\sum_i P_i \ln P_i = -[P_1 \ln P_1 + (1 - P_1)\ln(1 - P_1)]$$

where we have used the fact that $P_1 + P_2 = 1$. We use the principle of maximum uncertainty and set the derivative of S with respect to P_1 equal to zero

$$\frac{dS}{dP_1} = -[\ln P_1 + 1 - \ln(1 - P_1) - 1] = -\ln\left(\frac{P_1}{1 - P_1}\right) = 0 \Rightarrow \frac{P_1}{1 - P_1} = 1 \Rightarrow P_1 = 1/2$$

8.2.3 The Rules of Probability

We will now present the basic rules of probability. Suppose that we know that the probability of rolling any face of a die in one throw is equal to 1/6 and we want to find the probability of finding face *3* or face *6* in one throw. In this case, we wish to know the probability of a trial that is a combination of more elementary operations for which the probabilities are already known. That is, we want to know the probability of the outcome, *i* or *j*, where *i* and *j* are mutually exclusive events. According to the rules of probability, the probability of event *i* or *j* is given by

$$P(i \ or \ j) = P(i) + P(j)$$

This is known as the **addition rule** and it is generalizable to more than two events. An important consequence of the addition rule is that if $P(i)$ is the probability of event *I*, then the probability of event *i* not occurring is $1 - P(i)$.

Another simple rule concerns the probability of the joint occurrence of independent events. Events are independent if the occurrence of one event does not affect the probability of the occurrence of the other. These events might be the probability of throwing a *3* on one die *and* the probability of throwing a *4* on a second die. If the two events are independent, then the probability of both events occurring is the product of their probabilities

$$P(i \ and \ j) = P(i)P(j)$$

This is known as the **multiplication rule.**

8.3 Random Variables and Probability Distributions

Broadly speaking, there are two kinds of processes: deterministic and random. For a **deterministic process**, the outcome of each experiment is set or can be determined through some physical law (i.e. using Newton's laws to determine the position of a particle). For a **random process** (also called a **stochastic process**), the outcome of each experiment is not

known and thus there are several potential outcomes for each experiment (which are defined by the sample space of the experiments). If each value in the same space has a well-defined probability, then we can define a **random variable** for the system. Thus in mathematical terms, a random variable is understood as a function defined on a sample space whose outputs are numerical values. A random variable can take on a set of possible different values within the sample space of the system, each with an associated probability. A random variable's possible values might represent the possible outcomes of a yet-to-be-performed experiment, or the possible outcomes of a past experiment whose already-existing value is uncertain.

There are two types of random variables: discrete and continuous. A **discrete random variable** is one which may take on only a countable number of distinct values. Thus, if a random variable can take only a finite number of distinct values, then it must be discrete. Examples of discrete random variables include the number of children in a given family, the number of patients in a doctor's surgery, the number of heads obtained by flipping 20 coins, and the number of defective light bulbs in a box of 10. A **continuous random variable** is one which takes an infinite number of possible values. Continuous random variables are usually measurements such as the time required to run a mile.

The mathematical function that relates the possible values of a random variable to their associated probabilities is known as a **probability distribution function**. Suppose a random variable X may take k different values with the probability that $X = x_i$ defined to be $P(X = x_i) = p(i)$. The probabilities must satisfy the same conditions mentioned earlier:

$$P(i) \geq 0, \quad \sum_i P(i) = 1$$

In many cases of physical interest, the random variables have continuous values, such as the position and velocity of a particle described by classical mechanics. Another example of a continuous random variable is the displacement from the origin of a one-dimensional random walker that steps at random to the right with probability p, but with a step length that is chosen at random between zero and the maximum step length a. The continuous nature of the step length means that the displacement x of the walker is a continuous random variable. If we perform a simulation of this random walk, we can record the number of times $H(x)$ that the displacement of the walker from the origin after N steps is in a bin of width Δx between x and $x + \Delta x$. To obtain the probability, we divide $H(x)$ by the total number of walkers N_w.

Because we expect the number of walkers in a particular bin to be proportional to the width of the bin, we may write $p(x)\Delta x = H(x)/N_w$. The quantity $p(x)$ is called the **probability density**. In the limit $\Delta x \to 0$, $H(x)$ becomes a continuous function of x, and we can write the probability that the displacement x of the walker is between a and b as

$$P(a < x < b) = \int_a^b p(x)dx$$

Note that the probability density $p(x)$ is nonnegative and has units of one over the dimension of length. Moreover, the normalization condition for the probability density function is given by

$$\int_{-\infty}^{\infty} p(x)dx = 1$$

8.4 Mean Values and Variance

The specification of the probability distribution for the possible values of the random variable x constitutes the most complete statistical description of the system. However, in many cases, it is more convenient to describe the distribution of the possible values of x in a less detailed way. The most familiar way is to specify the **average** or **mean** value of x, which we will denote as $\langle x \rangle$. The definition of the mean value of x is

$$\langle x \rangle = \sum_{i=1}^{n} x_i P_i \rightarrow \int_{-\infty}^{\infty} xP(x)\,dx$$

where $P(i)$ is the probability of x_i. If $f(x)$ is a function of x, then the mean value of $f(x)$ is given by

$$\langle f(x) \rangle = \sum_{i=1}^{n} f(x_i)P_i \rightarrow \int_{-\infty}^{\infty} f(x)P(x)\,dx$$

If $f(x)$ and $g(x)$ are any two functions of x, then

$$\langle f(x) + g(x) \rangle = \langle f(x) \rangle + \langle g(x) \rangle$$

We define the ***m*th moment** of the probability distribution P as

$$\langle x^m \rangle = \sum_{i=1}^{n} x_i^m P_i \rightarrow \int_{-\infty}^{\infty} x^m P(x)\,dx$$

where we have let $f(x) = x^m$. Thus, the mean of x is the first moment of the probability distribution.

The mean value of x is a measure of the central value of x about which the various values of x_i are distributed. If we measure the deviation of x from its mean, we have

$$\Delta x \equiv x - \langle x \rangle, \quad \langle \Delta x \rangle = \langle x \rangle - \langle \langle x \rangle \rangle = 0$$

That is, the average value of the deviation of x from its mean vanishes.

If only one outcome j were possible, we would have
$$P_i = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}$$

that is, the probability distribution would have zero width. Usually, there is more than one outcome and a measure of the width of the probability distribution is given by

$$\langle \Delta x^2 \rangle \equiv \langle (x - \langle x \rangle)^2 \rangle$$

The quantity $\langle \Delta x^2 \rangle$ is known as the **dispersion** or **variance** and its square root is called the **standard deviation**. The use of the square of Δx ensures that the contribution of x values that are smaller and larger than $\langle x \rangle$ contribute to $\langle \Delta x^2 \rangle$ with the same sign. It's easy to see that the larger the spread of values of x about $\langle x \rangle$, the larger the variance. A useful form for the variance can be found by noting that

$$\langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle\langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$$

Because $\langle \Delta x^2 \rangle$ is always nonnegative, it follows that $\langle x^2 \rangle \geq \langle x \rangle^2$.

The variance is the mean value of $(x - \langle x \rangle)^2$ and represents the square of a width. We will find that it is useful to interpret the width of the probability distribution in terms of the standard deviation σ, which is defined as the square root of the variance. The standard deviation of the probability distribution $P(x)$ is given by

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

8.5 Binomial Distribution

In this section, we will examine two-state systems and examine the probability distribution of these systems. From our above example of flipping coins, we see that there are

only two possible outcomes for each trial (either heads or tails). Second, we see that the result of each trial is independent of all previous trials. This type of process is called a **Bernoulli process**. Let's examine the probability of determining n heads for N coins: $P(N, n)$.

First, let's call the probability of getting heads p and the probability of getting tails $q = 1 - p$. We will call each individual outcome a **microstate** and we will call the particular outcome with n heads and $N - n$ tails a **macrostate**. Since the result of each trial is independent of all previous trials, then the probability of a particular outcome with n heads and $N - n$ tails occurs with probability $p^n(1 - p)^{N-n}$. However, we note that there are numerous ways in which we can obtain this. Thus, we can write the probability $P(N, n)$ as

$$P(N, n) = \Omega(N, n)p^n(1 - p)^{N-n}$$

where $\Omega(N, n)$ is the number of distinct microstates of N coins with n heads and $N - n$ tails. The quantity is also called the **multiplicity** of that macrostate.

We can determine the general form of $\Omega(N, n)$ as follows: suppose we lined up N coins in a row and we ask how many ways we can arrange n heads (where $n < N$). Start with the first coin with a heads, there are N ways to arrange it. After fixing the first coin with a heads, then there will be $N - 1$ ways to arrange the second coin. After fixing the first two coins with heads, then there will be $N - 2$ ways to arrange the third coin. If we continue this process for n coins with a heads, then we will have $N(N - 1)(N - 2) \dots (N - n + 1)$ total ways to arrange them. In the language of combinatorics, this result is known as a **permutation** of N coins selected n at a time**.** A permutation is the number of possible arrangements of all objects of a collection into a distinct order.

However, in our original problem, we are not concerned about the individual arrangement of each individual coin with a heads. Rather, we are interested in determine the number of unique collections of n coins with heads from a group of N coins. In other words, we do not care about the arrangement of each coin with heads within the collection of n coins. In mathematical terms, this means that we are assuming that the individual coins within the collection of n coins are indistinguishable. Hence, we need to correct for the overcounting that occurs when counting indistinguishable coins within a group of n heads. Fortunately, this can be done using the same essential method as above. If we have n coins with heads, then there will $n(n - 1)(n - 2) \dots = n!$ ways to arrange them within the group. Thus, the total number of unique collections of n coins with heads out of N total coins is given by

$$\Omega(N,n) = \frac{N(N-1)(N-2)\dots(N-n+1)}{n!} = \frac{N(N-1)(N-2)\dots(N-n+1)(N-n)!}{n!\,(N-n)!}$$

$$= \frac{N!}{n!\,(N-n)!} \equiv \binom{N}{n}$$

In the language of combinatorics, this result is known as a **combination.** A combination is the number of possible ways in which items can be selected from a collection such that (unlike permutations) the order of selection does not matter. Therefore, the probability of determining n heads for N coins is given by

$$P(N,n) = \binom{N}{n} p^n (1-p)^{N-n} \qquad (8.1)$$

Equation (8.1) is a special type of probability distribution known as the **binomial distribution**. For our particular example, $p = 1/2$ and thus, $P(N,n)$ reduces to

$$P(N,n) = \binom{N}{n} 2^{-N}$$

The probability $P(N,n)$ is shown in Figure 8.2
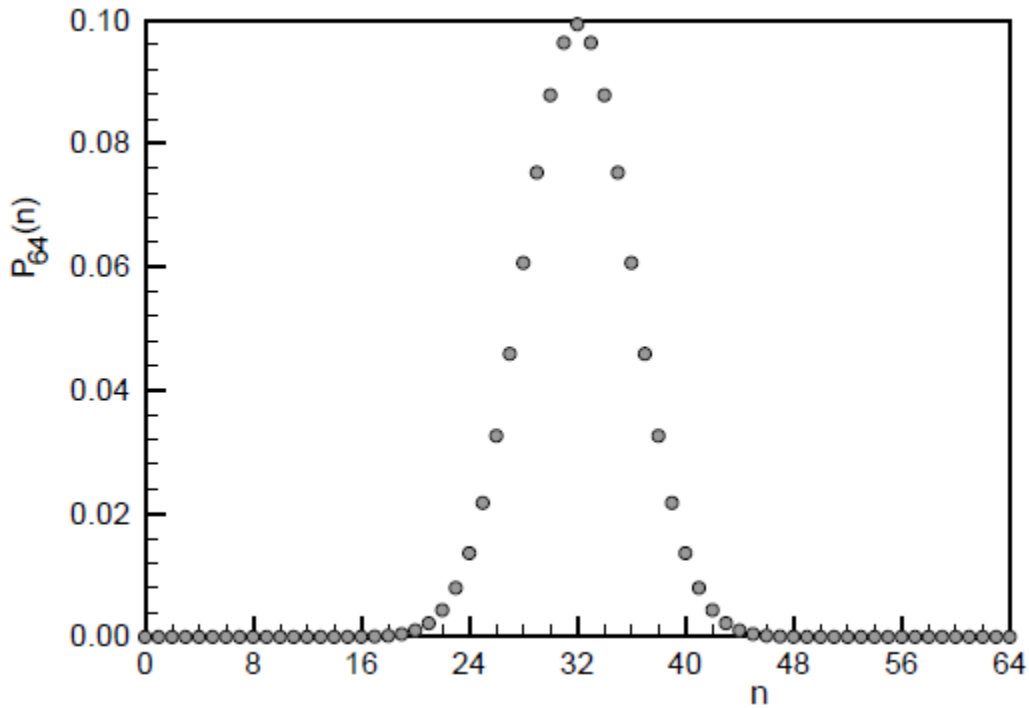
Figure 8.2 The binomial distribution for $N = 64$ and $p = 1/2$

205

Now that we have the probability distribution, we can calculate the mean and variance of the distribution. From the definition of the mean value, we have

$$\langle n \rangle = \sum_{n=0}^{N} n\, P(N,n) = \sum_{n=0}^{N} \frac{nN!}{n!\,(N-n)!} p^n (1-p)^{N-n}$$

We can evaluate the sum above using a technique that is useful in a variety of contexts. The technique is based on the fact that

$$p\frac{d}{dp}p^n = np^n$$

We can rewrite $\langle n \rangle$ as

$$\langle n \rangle = \sum_{n=0}^{N} \frac{nN!}{n!\,(N-n)!} p^n (1-p)^{N-n} = \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} \left(p\frac{\partial}{\partial p}p^n\right)(1-p)^{N-n}$$

$$= p\frac{\partial}{\partial p}\left[\sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} p^n (1-p)^{N-n}\right]$$

By the binomial theorem, the term in the bracket is equal to $\left(p + (1-p)\right)^N$. If we let $q = 1 - p$, we have

$$\langle n \rangle = p\frac{\partial}{\partial p}\left[(p+q)^N\right] = pN(p+q)^{N-1} = pN$$

The variance can be calculated in a manner similar to that for the mean value. It can be shown that the variance is given by $\sigma_n^2 = p(1-p)N$. The relative width of the binomial distribution is given by

$$\frac{\sigma_n}{\langle n \rangle} = \frac{\sqrt{p(1-p)N}}{pN} = \left(\frac{1-p}{p}\right)^{1/2}\frac{1}{\sqrt{N}}$$

We note that the relative width goes to zero as $N^{-1/2}$.

Let's examine the behavior of the binomial distribution for large N. In order to accomplish this, we will need to evaluate $N!$ for $N \gg 1$. An approximation for $N!$ is known as Stirling's approximation is

$$\ln N! \approx N\ln N - N$$

We can use Stirling's approximation to provide a useful expression for the binomial distribution for large N. The first step is to realize that $P(N,n)$ for $N \gg 1$ is a rapidly varying function of n near the maximum of $P(N,n)$. For this reason, we do not want to approximately $P(N,n)$ directly. Because the logarithm of $P(N,n)$ is a slowly varying function, we expect that the Taylor series expansion of $\ln P(N,n)$ will converge. Hence we expand $\ln P(N,n)$ in a Taylor series about the value of $n = \tilde{n} = pN$ at which $\ln P(N,n)$ reaches its maximum value. We have

$$\ln P(N,n) = \ln P(N, n = \tilde{n}) + (n - \tilde{n})\left(\frac{d \ln P(N,n)}{dn}\right)_{n=\tilde{n}} + \frac{1}{2}(n - \tilde{n})^2\left(\frac{d^2 \ln P(N,n)}{d^2 n}\right)_{n=\tilde{n}}$$
$$+ \cdots$$

Because the expansion above is about the maximum $n = \tilde{n}$, then the first derivative must be zero and the second derivative must be negative. We assume that the higher order terms can be neglected and adopt the notation

$$\ln A = \ln P(N, n = \tilde{n}), \quad B = -\left(\frac{d^2 \ln P(N,n)}{dn^2}\right)_{n=\tilde{n}}$$

This notation allows us to write our expansion as

$$\ln P(N,n) \approx \ln A - \frac{1}{2}B(n - \tilde{n})^2 \Rightarrow P(N,n) \approx A \exp\left[-\frac{1}{2}B(n - \tilde{n})^2\right]$$

Next, we use Stirling's approximation to evaluate the first two derivatives of $\ln P(N,n)$ to find the parameters B and $\tilde{n}$. We have

$$\ln P(N,n) = \ln N! - \ln n! - \ln(N - n)! + n \ln p + (N - n) \ln q$$

$$\frac{d \ln P(N,n)}{dn} = -\ln n + \ln(N - n) + \ln p - \ln q$$

$$\frac{d^2 \ln P(N,n)}{dn^2} = -\frac{1}{n} - \frac{1}{N - n}$$

Therefore, we have for the coefficient B

$$B = -\left(\frac{d^2 \ln P(N,n)}{dn^2}\right)_{n=\tilde{n}} = \frac{1}{\tilde{n}} + \frac{1}{N - \tilde{n}} = \frac{1}{Npq} = \frac{1}{\sigma^2}$$

Moreover, it can be shown that for large N, the coefficient A becomes

$$A = \frac{1}{(2\pi Npq)^{1/2}} = \frac{1}{(2\pi\sigma^2)^{1/2}}$$

Therefore, the binomial distribution at large N can be written as

$$P(N, n) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(n - \tilde{n})}{2\sigma^2}\right]$$

This distribution is known as the **Gaussian probability distribution**. From our derivation, we see that Gaussian distribution is valid for large N and for values of n near its mean. The Gaussian approximation is a good approximation even for relatively small values of N for most values of n. The most important feature of the Gaussian probability distribution is that its relative width decreases as $N^{-1/2}$, just as the binomial distribution.

8.6 Central Limit Theorem

We have discussed how to estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent random events. Intuitively, we believe that if we perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called the law of large numbers. However, we can go further and find the form of the probability distribution that a particular measurement differs from the exact mean. The form of this probability distribution is given by the central limit theorem.

Suppose that we wish to estimate the probability of obtaining the face with five dots in one throw of a die. The answer of $1/6$ means that if we perform N measurements, five will appear approximately $N/6$ times. What is the meaning of "approximately"? Let S be the total number of times that a five appears in N measurements. We write

$$S = \sum_{i=1}^{N} s_i$$

where

$$s_i = \begin{cases} 1, & ith\ throw\ gives\ 5 \\ x, & otherwise \end{cases}$$

The ratio S/N approaches $1/6$ for large N. How does this ratio approach the limit? We can empirically answer this question by repeating the measurement M times. (Each measurement of S consists of N throws of a die.) Because S itself is a random variable, we know that the measured values of S will not be identical. In Figure 8.3, we show the results of $M = 10,000$

measurements of S for $N = 100$ and $N = 800$. We see that the approximate form of the distribution of values of S is a Gaussian.

This empirical result can be stated formally. In the limit $N \to \infty$, the probability density $p(S)$ is given by

$$p(S) = \frac{1}{\sqrt{2\pi\sigma_S^2}} \exp\left[-\left(\frac{S - \langle S \rangle}{2\sigma_S^2}\right)\right]$$

where $\langle S \rangle = Ns$ and $\sigma_S^2 = N\sigma^2$. The quantity $p(S)\Delta S$ is the probability that the value of the sum $\sum_{i=1}^{N} s_i$ is between S and $S + \Delta S$. This is the central limit theorem. Note that the Gaussian form above holds only for large N and for values of S near its most probable (mean) value. The latter restriction is the reason that the theorem is called the *central* limit theorem – the requirement that N be large is the reason for the term *limit*.
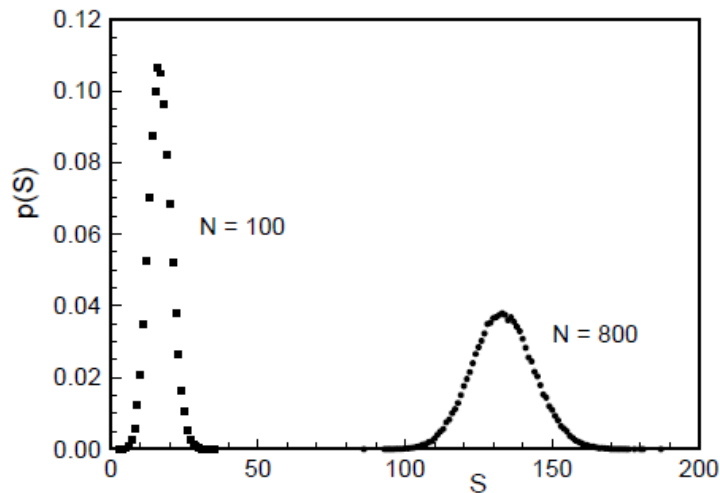
Figure 8.3 The distribution of the measured values of $M = 10,000$ different measurements of the sum S for $N = 100$ and $N = 800$ terms in the sum.

The central limit theorem is one of the most remarkable results of the theory of probability. In its simplest form, the theorem states that the probability distribution of the value of the sum of a large number of random variables is approximately a Gaussian. The approximation improves as the number of variables in the sum increases. The central limit theorem shows why the Gaussian probability density is ubiquitous in nature. If a random process is related to a sum of a large number of microscopic processes, the sum will be distributed according to the Gaussian distribution independently of the nature of the distribution of the microscopic processes.

The central limit theorem implies that macroscopic bodies have well defined macroscopic properties even though their constituent parts are changing rapidly. For example, the particle

positions and velocities in a gas or liquid are continuously changing at a rate much faster than a typical measurement time. For this reason we expect that during a measurement of the pressure of a gas or a liquid, there are many collisions with the wall and hence the pressure, which is a sum of the pressure due to the individual particles, has a well-defined average. We also expect that the probability that the measured pressure deviates from its average value is proportional to $N^{-1/2}$, where N is the number of particles. Similarly, the vibrations of the molecules in a solid have a time scale much smaller than that of macroscopic measurements, and hence the pressure of a solid also is a well-defined quantity.

8.7 The Methodology of Statistical Mechanics

We will now apply the tools and concepts of thermodynamics and probability which we introduced in the previous chapter to relate the microscopic and macroscopic descriptions of thermal systems. In so doing, we will develop the formulation of statistical mechanics. As mentioned in the previous chapter, the objective of statistical mechanics is to obtain all the equilibrium properties of macroscopic systems by applying the laws of mechanics and giving mechanical meaning to the thermodynamic variables. This is accomplished by combining mechanics with general statistical principles. Mechanics provides the general physical framework and statistics replaces the rigorous detail required by pure mechanics by general, reasonable, statistical assumptions whose validity can only be measured by experiment. The essential methodology of statistical mechanics can be summarized as follows:

1. Specify the macrostate and accessible microstate of the system
2. Choose the statistical ensemble that is appropriate for the system
3. Determine the mean values and other statistical properties of the system
4. Connect the statistical properties of the system to macroscopic thermodynamic variables of the system.

In this chapter, we will address the foundation principles that address this methodology and the implications of these principles. We begin by observing how to count the number of accessible microstates for several systems of interest.

8.7.1 Microstates and Macrostates

The state of any thermodynamic system is the set of all variables one needs to describe that system at any given time. Based on the previous sections, we now see that these are two kinds of variables, depending on the kind of description we are after:

- The **macrostate** of a system is the set of all macroscopic variables – variables that are actually measured in an experiment, such as the total energy, the pressure, the volume, the temperature, etc.
- The **microstate** of a system is the set of all variables of the system required for a complete [quantum] mechanical description of the system. These are the positions and momenta of each particle in the system (classical description) or the complete set of quantum numbers (quantum mechanical description) describing the wave-function of the system.

Generally speaking, a given macrostate will correspond to a huge number of allowable microstates. For example, if a macrostate is described only by the total energy and total number of particles of the system, there are a large number of ways in which this energy may be distributed between the particles to give the same total energy. Each of the ways corresponds to a given microstate. Thus, we define the number of microstates in a given macrostate as the **multiplicity**.

A microstate of a quantum mechanical system is completely given once its wavefunction is known and the wavefunction is given by f "quantum numbers", where f is the number of degrees of freedom of the system

$$\psi = \psi_{\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_f}(t, x_1, \ldots, x_N)$$

Classical microstates have a very different description. Recall that the initial conditions required to solve Newton's equation are the positions and momenta of each particle. Thus, in order to fully describe the classical microstate of a system of particles, we need to specify all the coordinates and momenta of the particles of the system. For example, if the system has f degrees of freedom, we must specify $2f$ "phase space" variables: f coordinates and f momenta. Now the coordinates and momenta can take on any real value and the set of real numbers is dense; therefore, the number of possible classical microstates of a system is uncountable. This unpleasant situation can be corrected by dividing thermodynamic phase space into cells of fixed area, agreeing that the state of the system is to be specified by saying that its momentum lies between $\vec{p}$ and $\vec{p} + d\vec{p}$ and its position between $\vec{r}$ and $\vec{r} + d\vec{r}$ where the represented point $(\vec{r}, \vec{p})$ is within a cell of area

$$\delta^f \vec{p}\, \delta^f \vec{r} = \delta\vec{p}_1 \delta\vec{p}_2 \cdots \delta\vec{p}_f \delta\vec{r}_1 \delta\vec{r}_2 \cdots \delta\vec{r}_f = h_o^f$$

Now the microstates are all countable. Clearly, the description becomes more accurate as we take the area of each cell to approach zero. Although we will not be able to take that limit, we will assume that h_o is "macroscopically small" but "microscopically large". What this means is that

we assume that *any* macroscopic volume in phase-space includes a very large number of fundamental cells of volume h_o^f. This is known as the **continuum approximation**.

Very often we will need to sum over all microstates. For example, if we want to find average values of mechanical variables we will need to sum over values of the variable corresponding to each microstate. Summing over quantum microstates is easy because these are discrete and countable, so we use the ordinary summation. Likewise, to sum over classical states, we must sum over the phase space cells of volume h_o^f, in principle taking the limit as $h_o \to 0$ in the end if possible. Thus

$$\sum_{cells} \delta^f \vec{p}\, \delta^f \vec{r} \to \lim_{h_0 \to 0} \frac{1}{h_o^f} \int_R d^f \vec{r}\, d^f \vec{p}$$

where R is some relevant region of phase-space.

8.7.2 Statistical Ensembles

Although it is true that for a given macrostate there generally exist a large number of possible microstates, all obeying the constraints that define the macrostate, the system itself of course can be in only one of these macrostates at any given time. We have, however, no way of knowing precisely which one of the possible microstates it occupies because we only know the value of the macroscopic variables. We could speak about this in terms of probabilities: with what probability does the system find itself in a given microstate at any given time? How would we answer such questions of probability? As demonstrated from the previous sections, since the way we estimate probability is based on sampling and experimentation, we must therefore imagine that we have a very large number of identical systems at our disposal to perform the same experiment simultaneously on each one of the systems. By identical we mean systems with the same number of degrees of freedom, governed by the equations of motion and subject to the same boundary conditions. Such an imaginary collection of identical systems is called an **ensemble**.

How large should our collection of identical systems be? It should be at least as large as the number of states available to the system subject to the initial constraints. We then perform the same experiment or set of experiments on each member of the ensemble to determine the microscopic state of that member. If there are N such identical systems and state r is found N_r times, then the probability that state r occurs in any experiment is $P_r = N_r/N$. For example, imagine that we know the total energy of the system only. An ensemble of identical systems would then consist of a large number of systems having the same energy.

Now suppose that we want to know something more about the system, for example some property Y. The property will not generally be the same in every microstate because the allowed microstates must only have the same energy so it will depend on the particular microstate the system is in. Because we cannot know the precise microstate the system is in, we ask for the mean value of the property Y, defined as

$$\langle Y \rangle = \sum_r Y_r P_r \rightarrow \int Y(p,r) P(p,r) \, d^3r \, d^3r$$

where subscript r refers to the given microstate of the system. Of course, Y may never actually take the value $\langle Y \rangle$ and will in general fluctuate about this average value. The variance or (statistical dispersion) of the observable will, defined by $\langle \Delta Y^2 \rangle$, measures how much the observable fluctuates in the ensemble. For the average value of any macroscopic variable to have significance, its statistical fluctuations must be small compared with its average value. This is generically true when the system is "sufficiently" large because of the central limit theorem.

As mentioned previously, a statistical ensemble is a collection of identical systems in the same equilibrium state. What *kinds* of systems and what equilibrium states we consider will depend upon the physical system and the processes that are of interest. As mentioned in chapter 1, a thermodynamic system can be classified based on how the environment affects the thermodynamic system. Open systems can exchange both matter and energy with its environment; closed systems can only exchange energy with its environment; and isolated systems can exchange neither energy nor matter with its environment. Therefore, if we plan to examine the statistical properties of thermodynamic systems, we need to compose statistical ensembles that reflect open, closed, and isolated systems.

In statistical mechanics, a collection of isolated systems that have achieved equilibrium is called a **microcanonical ensemble**. Since an isolated system exchanges neither particles or energy, macrostates within the microcanonical ensemble are defined by the number of particle they contain and their total energy (together with other specified external parameters). A collection of closed systems is in contact with a heat reservoir is called the **canonical ensemble**. Since a closed system is able to freely exchange energy by heat with a reservoir, the canonical ensemble is characterized by the temperature of the reservoir and the number of particles in the system. In the canonical ensemble, if we relax the condition that no matter is exchanged between the system and its reservoir, we obtain the **grand canonical ensemble**. Thus the grand canonical ensemble is a collection of open systems that is in contact with a heat reservoir. Since an open system is able to freely exchange energy and particles with a reservoir, the grand canonical ensemble is characterized by the temperature of the reservoir and the number of particles in the system and reservoir. We will discuss the properties of these ensembles in future chapters.

8.7.3 The Fundamental Postulate

In discussing statistical ensembles, we had to perform experiments on each member of the ensemble in order to determine the probabilities P_r. We cannot do this in practice, of course, and in order to make theoretical progress, we must make further assumptions about these probabilities. Such assumptions would have to be quite complex indeed if they were to attempt to describe general thermodynamic states and/or processes. However, we expect that they would greatly simplify for equilibrium states of isolated systems. This hope has proved to be justified for, as we shall see, a relatively simple assumption for such systems provides incredible insights and makes superb predictions for a wide variety of thermodynamic systems and processes. This is the fundamental postulate of statistical mechanics which states that

An isolated system in equilibrium is equally likely to be found in any one of its accessible states, that is $P_r = P_s$ for any two accessible states r and s.

This is also called the assumption of **equal a priori probabilities**, and lies at the very heart of statistical mechanics. In fact, we use assumptions like this all of the time without really thinking about them. Suppose that we were asked to pick a card at random from a well-shuffled pack. I think that most people would accept that we have an equal probability of picking any card in the pack. There is nothing which would favor one particular card over all of the others. So, since there are fifty-two cards in a normal pack, we would expect the probability of picking the Ace of Spades, say, to be 1/52. We could now place some constraints on the system. For instance, we could only count red cards, in which case the probability of picking the Ace of Hearts, say, would be 1/26, by the same reasoning. In both cases, we have used the principle of equal a priori probabilities. People really believe that this principle applies to games of chance such as cards, dice, and roulette. In fact, if the principle were found not to apply to a particular game most people would assume that the game was "crooked".

In statistical mechanics, we treat a statistical ensemble a bit like an extremely large game of cards. Each accessible state corresponds to one of the cards in the pack. The interactions between particles cause the system to continually change its state. This is equivalent to constantly shuffling the pack. Finally, an observation of the state of the system is like picking a card at random from the pack. The principle of equal a priori probabilities then boils down to saying that we have an equal chance of choosing any particular card. Another way to examine this postulate is through the principle of maximum uncertainty. Because we do not have detailed information about the behavior of any individual microstate, we are assuming maximum uncertainty about the behavior of individual microstates.

But, imagine trying to prove that the principle actually does apply to a game of cards. It is, unfortunately, impossible to prove with mathematical rigor that the principle of equal a priori probabilities applies to many-particle systems, much like it would be extremely difficult to prove

that the principle actually does apply to a game of cards. Over the years, many people have attempted this proof, and all have failed miserably. Not surprisingly, therefore, statistical mechanics was greeted with a great deal of scepticism when it was first proposed just over one hundred years ago. Nowadays, statistical mechanics is completely accepted by virtually all physicists simply because it works.

8.7.4 The H theorem

Consider, now, a statistical ensemble of systems made up of weakly interacting particles. Suppose that this ensemble is initially very far from equilibrium. If each system starts off in a particular stationary state (i.e., with a particular set of quantum numbers) then, in the absence of particle interactions, it will remain in that state forever. Hence, the ensemble will always stay far from equilibrium, and the principle of equal a priori probabilities will never be applicable. In reality, particle interactions cause each system in the ensemble to make transitions between its accessible "stationary" states. This allows the overall state of the ensemble to change in time. Let us label the accessible states of our system by the index r. We can ascribe a time dependent probability $P_r(t)$ of finding the system in a particular approximate stationary state r at time t. Of course, $P_r(t)$ is proportional to the number of systems in the ensemble in state r at time t. In general, P_r is time dependent because the ensemble is evolving towards an equilibrium state.

Consider now the quantity H (from which the theorem derives its name), which is the mean value of $\ln P_r$ over all accessible states.

$$H = \sum_r P_r \ln P_r$$

\noindent The H theorem tells us that if an isolated system is initially not in equilibrium, then it will evolve under the influence of particle interactions in such a manner that the quantity H always decreases. This process will continue until H reaches its minimum possible value. This would imply that the final equilibrium state of the system is equally likely to be found in any of one of its accessible states. This is the situation predicted by the principle of equal a priori probabilities. Another way to examine this principle is to note that H is closely related to the statistical uncertainty of a system. As a system involves towards the minimum value of H, this implies that it will also evolve towards the state of maximum uncertainty. Hence, the H theorem is essentially repeating the principle of maximum uncertainty discussed previously.

The proof of the H theorem is beyond the scope of the notes, but it guarantees that an isolated many particle system will eventually reach equilibrium, irrespective of its initial state. The typical time-scale for this process is called the **relaxation time**, and depends in detail on the nature of the inter-particle interactions. The principle of equal a priori probabilities is only valid

for equilibrium states. It follows that we can only safely apply this principle to systems which have remained undisturbed for many relaxation times since they were setup, or last interacted with the outside world. The relaxation time for the air in a typical classroom is very much less than one second. This suggests that such air is probably in equilibrium most of the time, and should, therefore, be governed by the principle of equal a priori probabilities. In fact, this is known to be the case. Consider another example. Our galaxy, the Milky Way, is an isolated dynamical system made up of about 10^{11} stars. In fact, it can be thought of as a self-gravitating "gas" of stars. At first sight, the Milky Way would seem to be an ideal system on which to test out the ideas of statistical mechanics. Stars in the Galaxy interact via occasional "near miss" events in which they exchange energy and momentum. Actual collisions are very rare indeed. Unfortunately, such interactions take place very infrequently, because there is an awful lot of empty space between stars. The best estimate for the relaxation time of the Milky Way is about 10^{13} years. This should be compared with the estimated age of the Galaxy, which is only about 10^{10} years. It is clear that, despite its great age, the Milky Way has not been around long enough to reach an equilibrium state. This suggests that the principle of equal a priori probabilities cannot be used to describe stellar dynamics. Not surprisingly, the observed velocity distribution of the stars in the vicinity of the Sun is not governed by this principle.

Now that we have properly formulated the statistical problem, we can now use the methodology of statistical mechanics to examine thermodynamic systems in the microcanonical ensemble in the next chapter.

Chapter 9: The Microcanonical Ensemble

A microcanonical ensemble is a collection of isolated systems that have achieved equilibrium in the same state. A system is isolated from its environment if it exchanges neither particles nor energy with it by heat and therefore microcanoncial ensembles are defined by the number of particles they contain and their total energy, together with other external constraints. According to the fundamental postulate of statistical mechanics, the probability of finding a member of the ensemble in a given microstate r is

$$P_r = \frac{1}{\Omega(U, N, X_\alpha)}, \quad U_r = U, \quad N_r = N$$

where $\Omega(U, N, X_\alpha)$ is the number of states accessible to the systems and X_α are other extensive parameters possibly defining the system, such as volume. We see that all configurations that are consistent with the energy and number of particles occur with equal probability.

For isolated systems, it is thus a knowledge of $\Omega(U, N, X_\alpha)$ that allows us to proceed in statistical physics and so it's worth spending a little time analyzing its behavior. In the previous chapter, we have explicitly calculated $\Omega(U, N, X_\alpha)$ for a few isolated systems. Here we will attempt to obtain physical intuition for the way it behaves during thermodynamic processes in which the systems remain isolated. Again, by the H theorem, we know that $\Omega(U, N, X_\alpha)$ is related to entropy. This will allow us to make the connection between the number of states and the temperature, pressure, and "generalized forces" of isolated systems.

9.1 The Behavior of the Number of Microstates

As mentioned previously, if we had a system in a well-defined macrostate, defined by external parameters $X_1, \ldots, X_N$, the number of these microstates will be given as $\Omega = \Omega(U, N, X_1, \ldots, X_N)$ where U is the internal energy and N is the number of constituents of the system. The system is kept in a definite macrostate by the imposition of external constraints. For example, consider a gas in an insulated cylinder with a piston at one end. The macrostate is defined by giving the number of particles, the internal energy and the volume of the gas in the cylinder. The volume of the cylinder is maintained by keeping the position of the piston fixed.

If some of the constraints are removed, the external parameters change accordingly. The system is not in equilibrium immediately after the constraint is removed because the release of one constraint has allowed the system to access a much larger number of states, yet at the instant the constraint is removed it occupies only a fraction of them. Let's see how this works for the

number of states occupied by the ideal gas. Imagine that the gas is allowed to freely expand to some final volume V_f. We know from experience that the final volume will be larger than the initial volume (experimentally, an isolated gas never spontaneously contracts) but, because the expansion is free and the system is isolated, the internal energy stays the same. Again, because the gas expands the number of states accessible to it clearly increases.

What happens to the number of microstates available to an isolated system when a new equilibrium is reached after *any* thermodynamic process? The *H* theorem guarantees that the number of states will increase or stay the same but never decrease. If the process resulted from the release of a constraint, let the constraint which keeps the macroscopic variables X_α constant be released so that the value of X_α changes. Corresponding to this new equilibrium there will be either the same or a larger number of states than the initial macrostate allowed, and each state, say r, will correspond to a certain value of the parameter X_α, say X_{α_r}. In other words, X_α will have a certain average value

$$\langle X_\alpha \rangle = \frac{\sum_r \Omega\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N; X_{\alpha_r}\right) X_{\alpha_r}}{\Omega\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N\right)}$$

where $\Omega\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N; X_{\alpha_r}\right)$ is the number of accessible states when the macrostate is defined by $X_1, \dots, X_N$ *excluding* X_α and in which X_α admits the value of X_{α_r}. Evidently, $\Omega\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N; X_{\alpha_r}\right)$ must be peaked at the average value, $\langle X_\alpha \rangle$ of X_α. If it is not, then the statistical dispersion of X_α would be large, and every time we performed a measurement we would be likely to find a significantly different value of X_α. However, we find experimentally that the dispersion about the mean value is in fact very small compared to the mean value is in fact very small compared to the mean value itself. In other words, when one or more constraints on an isolated system are removed, the system evolves to a new equilibrium in which

- The number of accessible microstates has either increased or stayed the same, $\Omega_f\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N\right) \geq \Omega_i\left(X_1, \dots, \hat{X}_\alpha, \dots, X_N\right)$ and
- If X_α represents the constraint that has been removed, the new number of microstates is sharply peaked about the new average value of X_α

If $\Omega_f > \Omega_i$, simply reimposing the constraints on the isolated system will not in general reduce the number of states to the original value Ω_i Two examples will illustrate this:

1. Imagine a gas in an insulated box with a partition in it so that the gas occupies only one half of the box. The partition is a constraint that keeps the volume occupied by the gas fixed. Removing this constraint allows the gas to occupy the entire box which increases

the number of accessible microstates by essentially allowing it to double its volume. Replacing the partition does not cause the gas to return to its original state.

2. Consider a gas in an insulated cylinder with a piston at one end. At some initial time, let the macrostate be given by the total energy and the volume of the gas. The volume of the gas is maintained fixed by holding the position of the piston secure. Releasing the piston will obviously change its volume, its macrostate and the number of accessible states. Again, simply compressing the gas will not return it to its original state.

Of course, in each case, the gas can be returned to its original state, but the steps involved include interactions with the environment and the systems are no longer isolated. In the second example, for instance, we would have to place the cylinder in contact with a heat reservoir at a fixed temperature (equal to the initial temperature of the gas in the cylinder) and compress the piston till the gas achieves its original volume. Compression will tend to increase the internal energy of the gas, but it will give up this energy to the heat reservoir in order to maintain its temperature. The system consisting only of the gas in the cylinder has been returned to its initial state, but the larger system which includes the heat reservoir has received heat from the gas, and external work has been done on the gas, so the entire system has indeed changed. In fact the final number of states of the gas and its environment taken together (this is the isolated system during the process) has either increased or stayed the same.

A similar process can be carried out to return the first system to its initial state (place a thin piston against the wall of the box on the right hand side and slowly compress the gas keeping it in contact with a heat reservoir). Again, the remarks made earlier in connection with the second system is applicable.

9.2 Thermodynamics in the Microcanonical Ensemble

We will now examine the basic macroscopic (observable) variables and the laws of thermodynamics from the perspective of the microcanonical ensemble.

9.2.1 Absolute Temperature
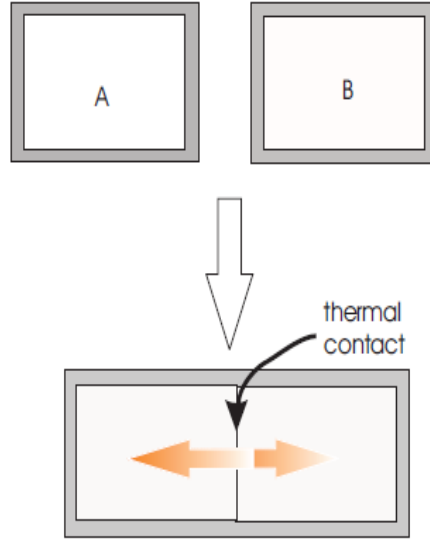
Figure 9.1 Schematic of two isolated systems brought into thermal contacts

Consider now two systems, A and B, and the system obtained by placing A and B in thermal contact with each other so that energy can be exchanged between them but only by heat, as shown in Figure 9.1. We will refer to this system as the composite system. Since A and B interact thermally they are individually not isolated, but we will assume that the composite system is isolated. At the moment they are brought into thermal contact with each other, if they are not already in equilibrium then they will exchange energy until they eventually achieve equilibrium. Furthermore, the process of heat exchange is a transformation that will, in general, increase the number of states available to the system as a whole. Equilibrium will be reached when the number of states is maximized.

Consider the final equilibrium situation. The total energy will be $U_{total} = U_A + U_B$ where U_A and U_B are the energies respectively of A and B (not necessarily known). U_{total} is fixed by the fact that the composite system is isolated, so the number of states of the composite system in which system A has energy U_A is

$$\Omega(U_{total}, U_A) = \Omega_A(U_A)\Omega_B(U_{total} - U_A)$$

However, because only the total energy is fixed and not the energy of A by itself, the total number of states accessible to the system will be a sum over all the possible values of U_A

$$\Omega(U_{total}) = \sum_{U_A} \Omega_A(U_A)\Omega_B(U_{total} - U_A)$$

What, then, is the probability of finding a given value, say U, for the energy of A? This is simply the ratio of the number of states of the composite system in which A has energy U_A divided by the total number of states available to composite system,

$$P(U) = \frac{\Omega_A(U)\Omega_B(U_{total} - U)}{\sum_{U_A}\Omega(U_{total}, U_A)} = C\Omega_A(U)\Omega_B(U_{total} - U)$$

where the denominator is some constant C^{-1} representing the total number of states available to the composite system. Taking logarithms on both sides, we have

$$\ln P(U) = \ln C + \ln \Omega_A(U) + \ln \Omega_B(U_{total} - U)$$

Now, in equilibrium, the number of microstates must be a maximum. At this stage, the energy of one of the systems, say A, will be $\tilde{U}$ and the other system B will have energy $\tilde{U}' = U_{total} - U'$. We therefore want $P(\tilde{U})$ to be maximum, which implies

$$\left.\frac{\partial \ln \Omega_A(U)}{\partial U}\right|_{\tilde{U}} + \left.\frac{\partial \ln \Omega_B(U_{total} - U)}{\partial U}\right|_{\tilde{U}} = 0$$

If we let the energy of system B be U', then we have

$$\left.\frac{\partial \ln \Omega_A(U)}{\partial U}\right|_{\tilde{U}} = \left.\frac{\partial \ln \Omega_B(U')}{\partial U'}\right|_{\tilde{U}'}$$

Since the system is in thermal equilibrium, this implies that the thermodynamic temperature must be related to $\partial \ln \Omega_A(U)/\partial U$. By dimensional analysis, we have

$$\frac{1}{kT_A} = \frac{1}{kT_B} \Rightarrow \beta(T_A) = \beta(T_B)$$

where k is the Boltzmann's constant and

$$\beta = \frac{1}{kT} = \frac{\partial \ln \Omega_A(U)}{\partial U} \Rightarrow T = \frac{1}{k}\left(\frac{\partial \ln \Omega_A(U)}{\partial U}\right)^{-1}$$

We have therefore seen that for two systems to be in equilibrium their absolute temperatures must be the same and so justified the thermodynamic concept of temperature, which asserts that temperature is that variable which determines whether or not two systems will be in thermal equilibrium: this is just the zeroth law of thermodynamics.

The absolute temperature also determines the direction of heat flow when two or more systems are brought into thermal contact. Consider the same system as before, observed in Figure 9.1. Heat will therefore flow from A to B (or vice versa) but no heat will leave the composite system. During the exchange process, the number of states of the composite system will increase. Therefore, when the systems are brought together, the number of states of the composite system is

$$\Omega(U_{total}) = C\Omega_A(U_i)\Omega_B(U_{total} - U_i)$$

\noindent Since the number of states is increasing,

$$d\ln\Omega(U) = \left(\frac{\partial \ln \Omega_A}{\partial U}\right)_{U_i}(U - U_i) + \left(\frac{\partial \ln \Omega_B}{\partial U'}\right)_{U_i'}(U' - U_i') \geq 0$$
$$\Rightarrow \beta_A(U_i)(U - U_i) + \beta_B(U' - U_i') \geq 0$$

Now, since the composite system is isolated, the total energy must stay fixed through any exchange of heat between A and B. In other words, whenever energy is gained (lost) by A is lost (gained) by B. Therefore, we have

$$[\beta_A(U_i) - \beta_B(U_i')](U - U_i) \geq 0$$

It follows that if $\beta_A > \beta_B$, then $U > U_i$ and energy flows from B to A. On the other hand, if $\beta_A < \beta_B$, then $U < U_i$ and energy flows from A to B. Since β is inversely proportional to the absolute temperature, it follows that energy flows from the body at a higher temperature to the one with the lower temperature.

9.2.2 Generalized Forces and Internal Energy

In our discussion of temperature, we examined the behavior of the number of states in systems with thermal interactions so that we could concentrate only on changes in the internal energy of the systems due to energy transfer by heat. More general interactions involve changes in the external parameters as well.

Consider a macroscopic system undergoing an *arbitrary* process and label *all the possible* microstates available to the system by r. Call the probability with which microstates r is occupied P_r. If some states are not accessible in the initial state, the occupation probabilities corresponding to those microstates will be identically zero. During the process, the states have characteristic energies, U_r, which will depend on the external parameters $X_1, \dots, X_N$. If some or

all of these macroscopic parameters, X_α, change during the process, the energy corresponding to the state r will change accordingly. Likewise, the probability that the system will be in state r will in general change. Because of these changes, the average energy of the system will change according to

$$dU = d\langle U \rangle = \sum_r dU_r P_r + \sum_r U_r dP_r$$

If the system is isolated during the quasi-static process, it will always obey the fundamental postulate because it never goes out of equilibrium. Therefore, $P_r = \Omega^{-1}$ will remain constant throughout the process and the second term on the right hand side will vanish. The first term on the right hand side is thus associated with the external work done by the system

$$\delta W = \sum_r dU_r P_r \quad (9.1)$$

Of course, if the system is not isolated during the process, the second term is nonvanishing and can be associated with energy transfer by heat:

$$\delta Q = \sum_r U_r dP_r$$

Therefore, we have the formal result $dU = \delta W + \delta Q$, which is simply the first law of thermodynamics. But now, statistical mechanics has given a microscopic meaning to the quantities that appear: ***macroscopic work is related to changes in the state energies and heat is related to change in the occupation probability distribution***.

Let's examine the expression for work. What Equation (9.1) says is that if the system does an amount of work δW_r, always staying in the state r, then the external work done by the system must be equal to the loss in energy of the state r. The change in the energy of the state r is

$$dU_r = \sum_\alpha \frac{\partial U_r(X_1, \dots, X_N)}{\partial X_\alpha} dX_\alpha \Rightarrow \delta W_r = -\sum_\alpha F_{\alpha,r} \, dX_\alpha$$

where $F_{\alpha,r} = -\partial U_r / \partial X_\alpha$. The macroscopic external work done is the average of the above,

$$\delta W = \sum_\alpha \left(\sum_r F_{\alpha,r} P_r \right) dX_\alpha = \sum_\alpha \langle F_\alpha \rangle dX_\alpha$$

223

The quantity $\langle F_\alpha \rangle$ is called the **generalized force** conjugate to **generalized coordinate** X_α – as mentioned previously in our discussion on thermodynamic potentials.

We can obtain a relationship between generalized forces and the number of states if we consider an infinitesimal quasi-static process during which $d\Omega(U, X_1, \ldots, X_N) = 0$. Because the number of states does not change, then

$$\frac{\partial \ln \Omega}{\partial U} dU + \sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha = 0 \Rightarrow \beta dU = -\sum_\alpha \frac{\partial \ln \Omega}{\partial X_\alpha} dX_\alpha$$

Furthermore because no energy is exchanged by heat, $dU = \delta W = -\langle F_\alpha \rangle dX_\alpha$. Comparison yields the relation

$$\langle F_\alpha \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \Omega}{\partial X_\alpha} \right)$$

Thus, if volume is the generalized coordinate that is changing for an isolated system, then pressure is the generalized force, which is related to the multiplicity function.

$$P = \frac{1}{\beta} \left(\frac{\partial \ln \Omega}{\partial V} \right)$$

9.2.3 Entropy

The thermodynamic entropy has the remarkable property that S of an isolated system can only increase or stay the same in any thermodynamic process, according to the second law. We have already discovered a quantity H, which satisfies an analogous property according to the H theorem. It makes sense therefore to simply adopt the following definition of entropy:

$$S = -kH = -k \sum_r P_r \ln P_r$$

where the sum is over all accessible states. Boltzmann's constant appears above only for convenience. The quantity H was introduced into gas kinetics by Boltzmann and later applied to general systems by Gibbs. Since $S = -kH$ it is called the **Boltzmann-Gibbs entropy**. For systems belonging to the microcanonical ensemble, we know that $H = -\ln \Omega$ and thus $S = k \ln \Omega$, where Ω is the multiplicity function. It satisfies the requirement that $\Delta S \geq 0$ during any process. In other words, entropy is the measure of statistical uncertainty in a given system and the second law of thermodynamics is essentially a statement of the principle of maximum uncertainty (this is why we labeled uncertainty with S).

Now consider a system initially belonging to the microcanonical ensemble and undergoing an arbitrary quasi-static process. For a small transformation immediately after the process begins, we can write

$$dS = k \, d\ln\Omega \approx k\left(\frac{\partial \ln\Omega}{\partial U}dU + \sum_\alpha \frac{\partial \ln\Omega}{\partial X_\alpha}dX_\alpha\right) = k\beta(dU + \delta W) \Rightarrow T \, dS = dU + \delta W$$

This is Gibbs equation which we saw earlier and it also gives us the thermodynamic definition of entropy

$$dS = \frac{\delta Q}{T}$$

In summary, we have succeeded not only in obtaining the thermodynamic laws, but also in acquiring a sense of the microscopic significant of some important everyday thermodynamic variables. Before proceeding to describe specific thermodynamic systems, let us first collect the important relations we have derived for the microcanonical ensemble.

$$\beta = \frac{1}{kT} = \frac{\partial \ln\Omega}{\partial U}$$
$$\langle F_\alpha \rangle = \frac{1}{\beta}\frac{\partial \ln\Omega}{\partial X_\alpha}$$
$$\delta W = -\sum_\alpha \langle F_\alpha \rangle \, dX_\alpha$$
$$S = -k\ln\Omega$$

Recall that the relationship between entropy and temperature is given from Gibbs equation as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

Now we can get obtain an energy equation of state $U = U(T,V,N)$ for any system for which we have an explicit formula for the multiplicity. Thus, we've bridged the gap between statistical mechanics and thermodynamics. The basic procedure is as follows

1. Define the macrostates and microstates for the given thermodynamic system
2. Find $\Omega(U,V,N)$ for the given thermodynamic system
3. Evaluate the entropy using
$$S(U,V,N) = k\ln\Omega\,(U,V,N)$$
4. Evaluate the temperature using

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

5. Solve for $U = U(T, V, N)$

9.3 Thermal Behavior of Einstein Solid

In 1907, Einstein proposed a model that reasonably predicted the thermal behavior of crystalline solids. In this model, a crystalline solid containing N atoms that behaves as if it contained $3N$ independent quantum harmonic oscillators. Let's determine the internal energy, specific heat, and chemical potential for this system.

First, we must define the macrostates and microstates for our given system. According to quantum mechanics, each oscillator has a minimum energy (also called the ground state energy), $\hbar\omega/2$ so that the minimum energy of N oscillators would be $E_0 = N\hbar\omega/2$. Moreover, according to quantum mechanics, each harmonic oscillator can only store energy at discrete levels such that $U = E_0 + q\epsilon$, where q is the number of energy units for a given harmonic oscillator and $\epsilon = \hbar\omega$ is the amount of energy for each discrete energy level. Therefore, the quantum state is defined by the excitation levels of each of the oscillators of the system. Each *microstate* corresponds to a particular distribution of q quanta between the N oscillators and each *macrostate* is specified by the total energy of the system U and the number of oscillators N.
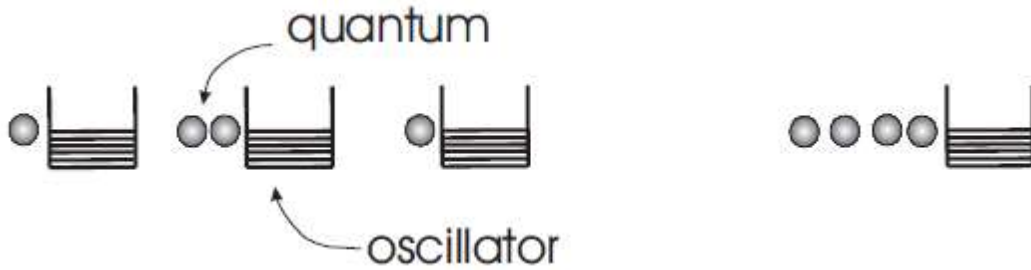
Figure 9.2: The oscillator problem

Next, we must determine the multiplicity function Ω for this given system. More specifically, we need to determine the multiplicity for a given macrostate with fixed energy quanta q and oscillators N. Since each microstate corresponds to a particular distribution of the q quanta between the N oscillators, a more pictorial way of formulating the problem (as shown in Figure 9.2) would be: in how many ways can q identical objects (the quanta) be distributed into N (identical) "boxes" (the oscillators) with no limit on the number of objects that can be put into each box? Since the last object of the distribution must be an oscillator (since each quantum is attached to a corresponding oscillator), we can rephrase the problem again as follows: In how many ways can we arrange q identical objects of one type and $N - 1$ identical objects of

another? Based on our discussion previously on combinatorics, our desired result is a combination of $q + N - 1$ objects selected q at a time. Therefore, the multiplicity of a given macrostate of fixed energy and oscillators is given by

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q! \, (N - 1)!}$$

For example, of there were only one quantum, it would have to go into some oscillator and there are N possibilities corresponding to number of ways in which the quantum is distributed between the oscillators. On the other hand, if there were $N = 100$ oscillators and $q = 4$ energy quanta then it can be shown that there are 4,424,275 possible microstates corresponding to this macrostate. In a normal solid, which can be thought of as a collection of oscillators (the molecules of the solid), each mole has on the order of $N_A = 10^{23}$ oscillators, so there are generally a huge number of microstates that correspond to any given macrostate of fixed energy and size.

Now that we have the multiplicity function, we can determine the relevant macroscopic variables of interest. Assuming a system with large N and large q, we can use Stirling's approximation to determine the entropy

$$
\begin{aligned}
S = k \ln \Omega = k \ln \left[\frac{(q + N - 1)!}{q! \, (N - 1)!} \right] &\approx k \ln \left[\frac{(q + N)!}{q! \, N!} \right] \\
&\approx k[(q + N) \ln(q + N) - (q + N) - q \ln q + q - N \ln N + N] \\
&= k \left[q \ln \left(\frac{q + N}{q} \right) + N \ln \left(\frac{N + q}{N} \right) \right]
\end{aligned}
$$

From the entropy, we can determine the temperature of an Einstein solid as a function of its internal energy:

$$
\begin{aligned}
\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} &= \frac{\partial S}{\partial q} \frac{\partial q}{\partial U} = \frac{1}{\epsilon} \frac{\partial S}{\partial q} = \frac{1}{\epsilon} \frac{\partial}{\partial q} [q \ln(q + N) - q \ln q + N \ln(q + N) - N \ln N] \\
&= \frac{k}{\epsilon} \left[\ln(q + N) + \frac{q}{q + N} - \ln q - \frac{q}{q} + \frac{N}{q + N} \right] \\
&= \frac{k}{\epsilon} \left[\ln(q + N) + \frac{q}{q + N} - \ln q - \frac{q}{q} + \frac{N}{q + N} \right] = \frac{k}{\epsilon} \ln \left(1 + \frac{N}{q} \right)
\end{aligned}
$$

Therefore, the temperature is

$$T = \frac{\epsilon}{k \ln(1 + N/q)} = \frac{\hbar \omega}{k \ln \left(1 + \frac{N}{q} \right)}$$

Thus, as expected, the temperature increases as the internal energy of the system increases. Rearranging the above expression to solve for internal energy gives (including the ground state energy

$$U = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\hbar\omega/kT} - 1} = \frac{N\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{kT}\right)$$

The heat capacity is therefore

$$C = \frac{\partial U}{\partial T} = -\frac{N\epsilon}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}\frac{\partial}{\partial T}\left[e^{\frac{\epsilon}{kT}}\right] = \frac{N\epsilon^2}{kT^2}\frac{e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2}$$

Let's examine the limiting cases for our solution. For the high temperature Einstein solid $(kT \gg \epsilon,\ q \gg N)$, we have

$$S = k\left[q\ln\left(\frac{q+N}{q}\right) + N\ln\left(\frac{N+q}{N}\right)\right] \approx kN\ln\left(\frac{q}{N}\right)$$

$$U = \frac{N\epsilon}{e^{\epsilon/kT} - 1} \approx \frac{N\epsilon}{1 - \frac{\epsilon}{kT} - 1} = NkT$$

$$C = \frac{N\epsilon^2}{kT^2}\frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} \approx \frac{N\epsilon^2}{kT^2}\frac{1 - \frac{\epsilon}{kT}}{\left(1 - \frac{\epsilon}{kT} - 1\right)^2} \approx \frac{N\epsilon^2}{kT^2}\frac{1}{\left(\frac{\epsilon}{kT}\right)^2} = Nk$$

At high temperature, we see that our results match the predictions of the equipartition theorem. For the low temperature Einstein solid $(kT \ll \epsilon,\ q \ll N)$, we have

$$S = k\left[q\ln\left(\frac{q+N}{q}\right) + N\ln\left(\frac{N+q}{N}\right)\right] \approx kq\ln\left(\frac{N}{q}\right)$$

$$U = \frac{N\epsilon}{e^{\epsilon/kT} - 1} \approx \frac{N\epsilon}{e^{\frac{\epsilon}{kT}}} = N\epsilon e^{-\epsilon/kT}$$

$$C = \frac{N\epsilon^2}{kT^2}\frac{e^{\epsilon/kT}}{(e^{\epsilon/kT} - 1)^2} \approx \frac{N\epsilon^2}{kT^2}\frac{e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}}\right)^2} = Nk\left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT}$$

Here, we see that both the energy and the specific heat approach zero at low temperatures. We will show at the end of this chapter that this is a consequence of the third law of thermodynamics.

The chemical potential is given by

$$\mu = -T\frac{\partial S}{\partial N} = -T\left[kq\left(\frac{1}{1+\frac{N}{q}}\right)\frac{1}{q} + k\ln\left(1+\frac{q}{N}\right) + kN\left(\frac{1}{1+\frac{q}{N}}\right)\left(-\frac{q}{N^2}\right)\right]$$

$$= -T\left[k\left(\frac{q}{q+N}\right) + k\ln\left(1+\frac{q}{N}\right) - k\left(\frac{q}{q+N}\right)\right] = -kT\ln\left(1+\frac{q}{N}\right)$$

In the limit $N \gg q$, the logarithm is approximately q/N, so $\mu \approx -qkT/N$. This says that when we add a "particle" to the system but no energy, the entropy increases by q/N (a number much less than 1). In the other limit, $N \ll q$, the logarithm is approximately $\ln(q/N)$. This is a significantly larger increase than in the first case. In other words, when there's already a large excess of particles over energy, adding another particle doesn't increase the entropy much. However, when there's an excess of energy units over particles, adding another particle gives a significant increase in entropy.

9.4 Thermal Behavior of Spin-1/2 Paramagnet
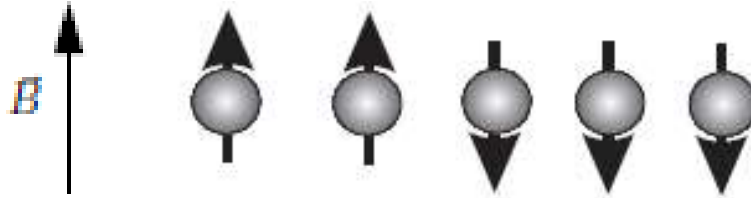
Figure 9.3 A collection of non-interacting magnetic dipoles in an external magnetic field

A **paramagnet** is a material in which the constituent particles (called **magnetic dipoles**) tend to align parallel to any external applied magnetic field. For any microscopic dipole, quantum mechanics only allows discrete values for the component of the dipole moment vector along any given axis. Consider an isolated paramagnetic system consisting of N non-interacting spin-1/2 particles, each possessing a magnetic moment $\vec{\mu}$, placed in an external magnetic field $\vec{B}$. For a spin-1/2 particle, only two values are allowed: spin "up" (which is aligned parallel to $\vec{B}$) and spin "down" (which is aligned antiparallel to $\vec{B}$). This implies that each "up" dipole has magnetic moment $+\mu$ and each "down" dipole has magnetic moment $-\mu$, where μ is a constant.

In a real-world paramagnet, the individual dipoles can be either electrons or atomic nuclei. Electronic paramagnetism occurs when there are electrons with angular momentum (orbital or spin) that is not compensated by other electrons; the circular currents then give rise to magnetic dipole moments. The number of possible states for each dipole is always some small integer, depending on the total angular momentum of all the electrons in an atom or molecule. The simple case considered here, with just two states, occurs when there is just one electron per atom whose spin is uncompensated. Ordinarily this electron would also have orbital angular

momentum, but in some environments, the orbital motion is "quenched" by the neighboring atoms, leaving only the spin angular momentum.

In order to examine the thermal properties of this system, we first have to define the microstates and macrostates of this system. The two basic macroscopic observables associated with this system are the total energy and the total magnetic moment (also called the **magnetization**). For this system, the magnetization is given by $\vec{M} = \vec{\mu}(N_\uparrow - N_\downarrow)$, where $N_\uparrow$ and $N_\downarrow$ are the numbers of up and down dipoles, respectively. Using electromagnetic theory, it can be shown that the energy of a single dipole in the external magnetic field is given by $\epsilon_i = -\vec{\mu}_i \cdot \vec{B}$. Assuming that each particle's dipole moment is constant, it can be shown that total energy of the system is $U = \mu B(N_\uparrow - N_\downarrow) = -\vec{M} \cdot \vec{B}$.

For this system, a particular *microstate* is specified if the direction of all spins is specified. Here the quantum state is specified by giving N quantum numbers (one component of the spin of each particle). Since each there are no interactions between the dipoles, there are 2^N possible distinct microstates and the probability of each microstate is $1/2^N$. A particular *macrostate* is specified by the total number of dipoles that point "up" (i.e. parallel to $\vec{B}$). Thus, to calculate the number of microstates corresponding to one macrostate of fixed energy and particle number, we need only to calculate the number of distinct arrangements of $N_\uparrow$ dipoles (i.e. the multiplicity of a given macrostate) out of N total dipoles. This system is mathematically equivalent to the binomial distribution and thus, the multiplicity is given by

$$\Omega(N, N_\uparrow) = \frac{N!}{N_\uparrow! \, N_\downarrow!}$$

If, instead we had 50 spin-1/2 particles and, knowing the total energy, we determined that 40 of them are spin up and 10 are spin down, there would be approximately 10^{10} microstates corresponding to this single macrostate.
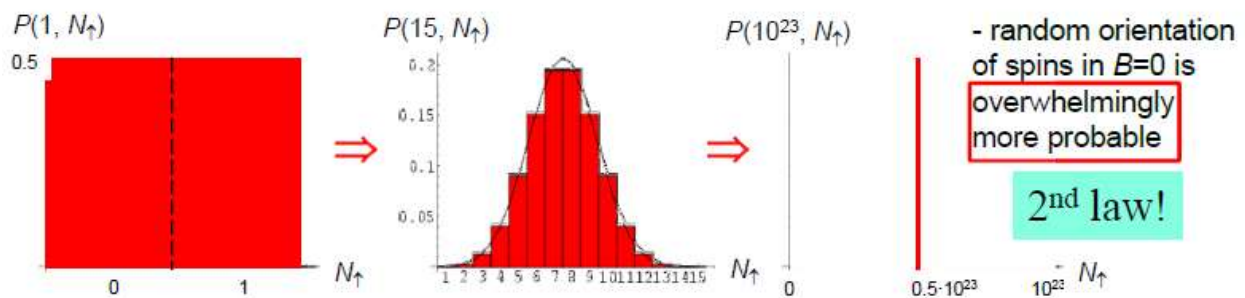
Figure 9.4 Plot of the probability distribution for the spin-1/2 paramagnetic system for 1 dipole (left), 15 dipoles (middle), and 10^{23} dipoles (right).

Therefore, the probability of macrostates of a two-state paramagnet in zero magnetic field is given by

$$P(N, N_\uparrow) = \frac{\Omega(N, N_\uparrow)}{2^N}$$

Note that as the system becomes larger, $P(N, N_\uparrow)$ becomes more sharply peaked, as shown in Figure 9.4. This implies that fluctuations about the mean are vanishingly small (a consequence of the central limit theorem). Moreover, note that for large N, there is a random orientation for the spins of the system. Therefore, the system has moved towards larger uncertainty as the number of dipoles has increased, indicating a large increase of entropy.

Now that we have the multiplicity function, we can determine the relevant macroscopic variables of interest. For large N, we can use Stirling's approximation to write the entropy of the two-state paramagnet as

$$S = k \ln \left[\frac{N!}{N_\uparrow! \, (N - N_\uparrow)!} \right] \approx kN \ln N - k N_\uparrow \ln N_\uparrow - k(N - N_\uparrow) \ln(N - N_\uparrow)$$

From the entropy, we can now calculate the temperature of the paramagnetic system

$$\frac{1}{T} = -\frac{1}{2\mu B} \frac{\partial S}{\partial N_\uparrow} = \frac{k}{2\mu B} \ln \left[\frac{N - U/\mu B}{N + U/\mu B} \right]$$

Solving for the internal energy U gives

$$U = N\mu B \left(\frac{1 - \exp[2\mu B/kT]}{1 + \exp[2\mu B/kT]} \right) = -N\mu B \tanh \left(\frac{\mu B}{kT} \right)$$

The specific heat can be determined based on the internal energy

$$C = \left(\frac{\partial U}{\partial T} \right)_{N,B} = Nk \frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)}$$

Based on the definition of magnetization, the magnetization is given by

$$M = N\mu \tanh \left(\frac{\mu B}{kT} \right)$$

In the high temperature limit in which $kT \gg \mu B$, we have

$$U = -N\mu B \tanh \left(\frac{\mu B}{kT} \right) \approx -\frac{N\mu^2 B^2}{kT}$$

$$M = N\mu \tanh \left(\frac{\mu B}{kT} \right) \approx \frac{N\mu^2 B}{kT}$$

$$C = Nk\frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)} \approx Nk\left(\frac{\mu B}{kT}\right)^2 = \frac{N\mu^2 B^2}{kT^2}$$

Unlike the Einstein solid, the internal energy of the system *decreases* as the temperature increases. This is consistent with the fact that the magnetization goes to zero for very high temperatures. The fact that $\langle M \rangle \propto 1/T$ was discovered experimentally by Pierre Curie and is known as **Curie's law**. Physically, we expect that, due to their thermal energy, there will be high randomness or lack of order in the system, and thus there will be relatively small amount of magnetic energy stored due to orientation of the dipoles in the system. Figure 9.5 shows the experimental values of a real paramagnet, compared to the prediction of Curie's law. Notice that the magnetization follows Curie's law very close down to a few Kelvins and that the experimental results deviate as the total magnetization approaches its maximum possible value.
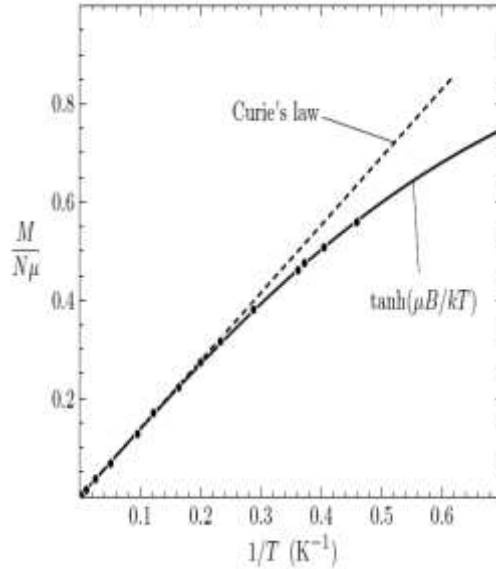
Figure 9.5 The magnetization of the spin-1/2 paramagnetic system for high temperatures

In the low temperature limit in which $kT \ll \mu B$, we have

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right) \approx -\mu NB$$

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right) \approx \mu B$$

$$C = Nk\frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)} \to 0$$

At very small temperatures, the system is completely magnetized. We expect that all the particles will be aligned in such a way as to minimize the total magnetic energy of the system. The

randomness in the orientation of spins induced by the thermal energy of the atoms is small compared with the order induced by the magnetic field.

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
100	−100	1.00	1	0	0	—
99	−98	.98	100	4.61	.47	.074
98	−96	.96	4950	8.51	.54	.310
97	−94	.94	1.6×10^5	11.99	.60	.365
⋮	⋮	⋮	⋮	⋮	⋮	⋮
52	−4	.04	9.3×10^{28}	66.70	25.2	.001
51	−2	.02	9.9×10^{28}	66.76	50.5	—
50	0	0	1.0×10^{29}	66.78	∞	—
49	2	−.02	9.9×10^{28}	66.76	−50.5	—
48	4	−.04	9.3×10^{28}	66.70	−25.2	.001
⋮	⋮	⋮	⋮	⋮	⋮	⋮
1	98	−.98	100	4.61	−.47	.074
0	100	−1.00	1	0	0	—
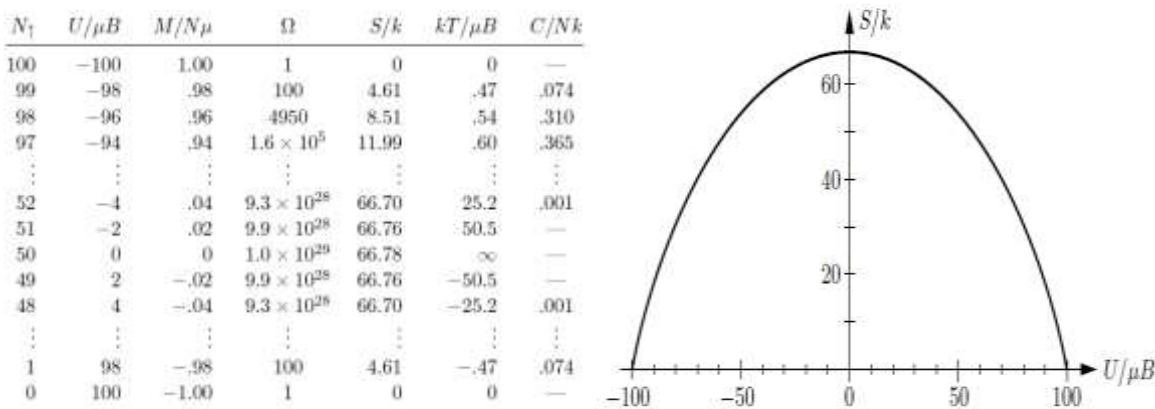
Figure 9.6 The magnetization of the spin-1/2 paramagnetic system consisting of 100 elementary dipoles

The thermal properties of a spin-1/2 paramagnet consisting of 100 elementary dipoles are given in Figure 9.6. The largest entropy occurs where $U = 0$ and as more energy is added to the system, the multiplicity and entropy actually *decrease*, since there are fewer ways to arrange the energy. This behavior is very different from that of a "normal" system such as an Einstein solid.

Let's look at this behavior in more detail. Suppose the system starts out in its minimum-energy state, with all the dipoles pointing up. Here the entropy-energy graph is very steep, so the system has a strong tendency to absorb energy from its environment. As its energy increases (but is still negative), the entropy-energy graph becomes shallower, so the tendency to absorb energy decreases, just as for an Einstein solid. However, as the energy of the paramagnet goes to zero, so does the slope of its entropy-energy graph, so its tendency to absorb more energy actually disappears. At this point, exactly half of the dipoles point down. If we add more energy to the system, the slope of its entropy-energy graph becomes negative, so it will spontaneously give up energy to any nearby object whose entropy-energy graph has a positive slope (remember, any allowed process that increases the *total* entropy will happen spontaneously.)

We can also think about the temperature of this system as a function of energy. When more than half of the dipoles point up, so the total energy is negative, this system behaves similar to the Einstein solid: its temperature (which is the reciprocal of the slope of the entropy-energy graph) increases as energy is added. When $U = 0$, however, the temperature is actually infinite, meaning that this system will give up energy to any other system whose temperature is finite. At higher energies, our definition of absolute temperature says that the temperature is negative (since the slope is negative). In this framework, negative temperature behave as if they are higher than positive temperatures since a system with negative temperature will give up energy to any system with positive temperature.

233

Generally speaking, negative temperatures can occur only for a system whose total energy is limited, so that the multiplicity decreases as the maximum allowed energy is approached. The best examples of such systems are **nuclear paramagnets**, in which the magnetic dipoles are the atomic nuclei rather than the electrons. In certain crystals the relaxation time for the nuclear dipoles (exchanging energy with each other) can be much shorter than the relaxation time for the nuclear dipoles to equilibrate with crystal lattice. Therefore, on short time scales, the dipoles behave as an isolated system with only magnetic energy. To give such a system a negative temperature, we would have to start with any positive temperature with most of the dipoles parallel to the magnetic field, then suddenly reverse the field so they're antiparallel. This experiment was first performed by Edward M. Purcell and R. V. Pound in 1951, using the lithium nuclei in a lithium fluoride crystal as the system of dipoles. In their original experiment the nuclear dipoles came to thermal equilibrium among themselves in only 10^{-5} seconds, but required approximately five minutes, after the field reversal, to return to equilibrium with the room-temperature crystal lattice. To learn more about nuclear systems with negative absolute temperature, see the following article:

http://www.physics.umd.edu/courses/Phys404/Anlage_Spring11/Ramsey-1956 Thermodynamics%20and%20S.pdf

9.5 Ideal Gas in the Microcanonical Ensemble

In this section, we examine the properties of the ideal gas within the framework of statistical mechanics in the microcanonical ensemble. Let's consider a gas of N non-interacting identical particles. Suppose that, besides the number of particles, we also know the total internal energy of the system, U. Because the energy of the system is simply the kinetic energy of the particles

$$U = \frac{1}{2m}\sum_{i=1}^{N}\vec{p}_i^2 \Rightarrow \sum_{i=1}^{N}\vec{p}_i^2 = 2mU$$

The above equation defines a 3N-dimensional hypersphere of radius $\sqrt{2mU}$. A hypersphere of radius R consists of the locus of points such that the distance from the origin is less than or equal to R. In our case, the above equation is the surface of a *3N* hypersphere in momentum space, which means that all of the momenta of the system are forced to reside on the surface of the hypersphere.

Recall that the multiplicity of any classical system can be written as

$$\lim_{h_0 \to 0} \frac{1}{h_o^f} \int_R d^f \vec{r} \, d^f \vec{p}$$

Since the energy equation forces the momenta to live on the surface of a hypersphere, the multiplicity of this system can be written as

$$\Omega(U,N,V) = \frac{1}{h_o^{3N}} \int_V d^{3N}\vec{r} \int d^{3N}\vec{p}\, \delta\left(\sum_{i=1}^{N} \vec{p}_i^2 - 2mU\right) = \frac{1}{h_o^{3N}} V^N \int d^{3N}\vec{p}\, \delta\left(\sum_{i=1}^{N} \vec{p}_i^2 - 2mU\right)$$

The multiplicity function describes the surface "area" of the $3N$ dimensional hypersphere. Therefore, to determine the multiplicity function, we must first determine the surface area of the $3N$ dimensional hypersphere. First, we note, by dimensional analysis, that the volume of this hypersphere is

$$V_{3N}(R) = \int dx_1 dx_2 \ldots dx_n = C_{3N} R^{3N}$$

where C_{3N} is the solid angle of the hypersphere. By the fundamental theorem of calculus, there is a relationship between the volume of the hypersphere and the surface area of the hypersphere

$$V_{3N}(R) = \int_0^R A_{3N-1}(r)\, dr \Rightarrow A_{3N-1}(R) = \frac{dV_{3N}(R)}{dR} = C_{3N-1} R^{3N-1}$$

To calculate this solid angle, we will do the following mathematical procedure. Consider the integral

$$I = \int_{-\infty}^{\infty} dx_1 dx_2 \ldots dx_d e^{-r^2}$$

We will evaluate this in two different ways. First, we simply write the integral as

$$I = \int_{-\infty}^{\infty} dx_1 dx_2 \ldots dx_d e^{-r^2} = \prod_{i=1}^{d} \int_{-\infty}^{\infty} dx_i e^{-x_i^2} = \prod_{i=1}^{d} (\sqrt{\pi}) = \pi^{d/2}$$

where we have used the common solution to the Gaussian integral. Let's evaluate the same integral using hyper-spherical coordinates, which gives

$$I = C_{d-1} \int_0^\infty r^{d-1} e^{-r^2} dr$$

If we define $t = r^2$, we have

$$I = \frac{C_{d-1}}{2} \int_0^\infty r^{\frac{d}{2}-1} e^{-t} dt \equiv \frac{C_{d-1}}{2} \Gamma\left(\frac{d}{2}\right)$$

where $\Gamma(x)$ is the Gamma function, which analytically continues the factorial function from the original domain of the natural numbers to the complex numbers: $\Gamma(n+1) = n!$. Comparing this value of the integral with the previous integral, we find

$$C_{d-1} = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)}$$

Therefore for a *3N* dimensional sphere with radius $R = \sqrt{2mU}$, its surface area is given by

$$A_{3N-1} = C_{3N-1} R^{3N-1} = \frac{2\pi^{\frac{3N-1}{2}}}{\Gamma\left(\frac{3N-1}{2}\right)} (2mU)^{\frac{3N-1}{2}}$$

Therefore, the multiplicity function is given by

$$\Omega(U,V,N) = \frac{1}{h_o^{3N}} V^N \int d^{3N}\vec{p}\, \delta\left(\sum_{i=1}^N \vec{p}_i^2 - 2mU\right) = \frac{1}{h_o^{3N}} \frac{2\pi^{\frac{3N-1}{2}}}{\Gamma\left(\frac{3N-1}{2}\right)} V^N (2mU)^{\frac{3N-1}{2}}$$

If we assume that we have a large number of particles in the box, then this may be approximated as

$$\Omega(U,V,N) \approx \frac{1}{h_o^{3N}} \frac{2\pi^{3N/2}}{\Gamma(3N/2)} V^N (2mU)^{3N/2}$$

Notice that the exponent of U in the above expression is $1/2$ times the total number of degrees of freedom *3N* in the monatomic gas. Now, in the microcanonical ensemble, we have assumed that every particle in the box is distinguishable from each other. However, from quantum mechanics, we know that particles in a box are indistinguishable from each other. To correct this inconsistency, we can include a factor of $1/N!$ to account for the overcounting of microstates. Therefore, our final multiplicity function is given by

$$\Omega(U,V,N) \approx \frac{1}{h_o^{3N}N!}\frac{2\pi^{3N/2}}{\Gamma(3N/2)}V^N(2mU)^{3N/2}$$

Now we have the multiplicity function, we can calculate the macroscopic variables of interest. First, we note that the external parameter of interest is the volume and the generalized force corresponding to this parameter is just the pressure. Thus, $\delta W = -P\, dV$ and we can calculate the pressure as

$$P = \frac{1}{\beta}\left(\frac{\partial \ln\Omega}{\partial U}\right) = \frac{1}{\beta}\left(\frac{N}{V}\right) = \frac{NkT}{V}$$

The entropy of a monatomic ideal gas is given by

$$S = k\ln\left(\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}(2mU)^{3N/2}\right) = k\left\{\ln V^N + \ln\left(\frac{2\pi mU}{h^2}\right)^{\frac{3N}{2}} - \ln N! - \ln\left[\left(\frac{3N}{2}\right)!\right]\right\}$$

$$= k\left\{N\ln V + N\ln\left(\frac{2\pi mU}{h^2}\right)^{\frac{3}{2}} - N\ln N + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}\right\}$$

$$= kN\left[\ln\frac{V}{N} + \ln\left(\frac{2\pi mU}{h^2}\right)^{\frac{3}{2}} - \ln\left(\frac{3N}{2}\right)^{\frac{3}{2}} + \frac{5}{2}\right] = Nk\left[\ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

The above result is known as the **Sackur-Tetrode equation**. Using the Sackhur-Tetrode equation, the temperature is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3Nk}{2U}$$

Therefore, the internal energy is given by

$$U(N,T) = \frac{3}{2}NkT$$

9.6 Heat and Irreversibility

We will use the framework of statistical mechanics to understand heat flow and the concept of irreversibility. We will accomplish this by examining the energy exchange between two interacting Einstein solids.

q_A	Ω_A	q_B	Ω_B	$\Omega_{total} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
				$462 = \binom{6+6-1}{6}$
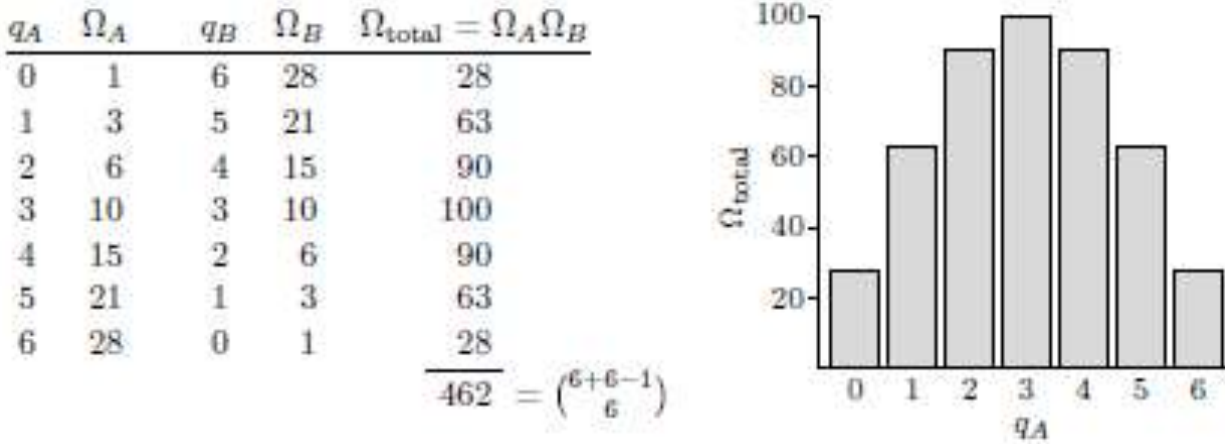
Figure 9.7 Macrostates and multiplicities of a system of two Einstein solids, each containing three oscillators, sharing a total of six units of energy.

Consider two Einstein solids that can exchange energy with each other and remain isolated from the rest of the universe. For simplicity, we will assume that the two solids are weakly coupled so that the exchange of energy between them is much slower than the exchange of energy among atoms within each solid. This implies that the individual energy of the solids, U_A and U_B, will change slowly and thus over sufficiently short time scales they are essentially fixed. Here the macrostate of the combined system is specified by the constrained values of U_A and U_B

For any macrostate we can compute the multiplicity. Let's start with a very small system, in which each of the "solids" contains only three harmonic oscillators and they contain a total of six units of energy: $N_A = 3 = N_B$ and $q_{total} = q_A + q_B = 6$. Given these parameters, the individual values of q_A or q_B must be specified to describe the macrostate of the system. There are seven possible macrostates with $q_A = 0, 1, \ldots, 6$ and since both solids are weakly coupled, the total multiplicity of any macrostate, Ω_{total}, is just the product of the individual multiplicities. The results of the system are given in Figure 9.7. As can be seen, the number of microstates accessible to the system is 462. If we invoke the fundamental assumption for our system of two small Einstein solids, we can immediately conclude that, while all 462 *microstates* are equally probable, some *macrostates* are more probable than others. For instance, the probability of finding the system in the fourth macrostate (with three energy units in each solid) is $100/462$, while the chance of finding it in the first macrostate (with all the energy in solid B) is only $28/462$. Thus, if all the energy is in solid B initially, then it is more probable that the energy will be distributed more evenly as the system approaches equilibrium.

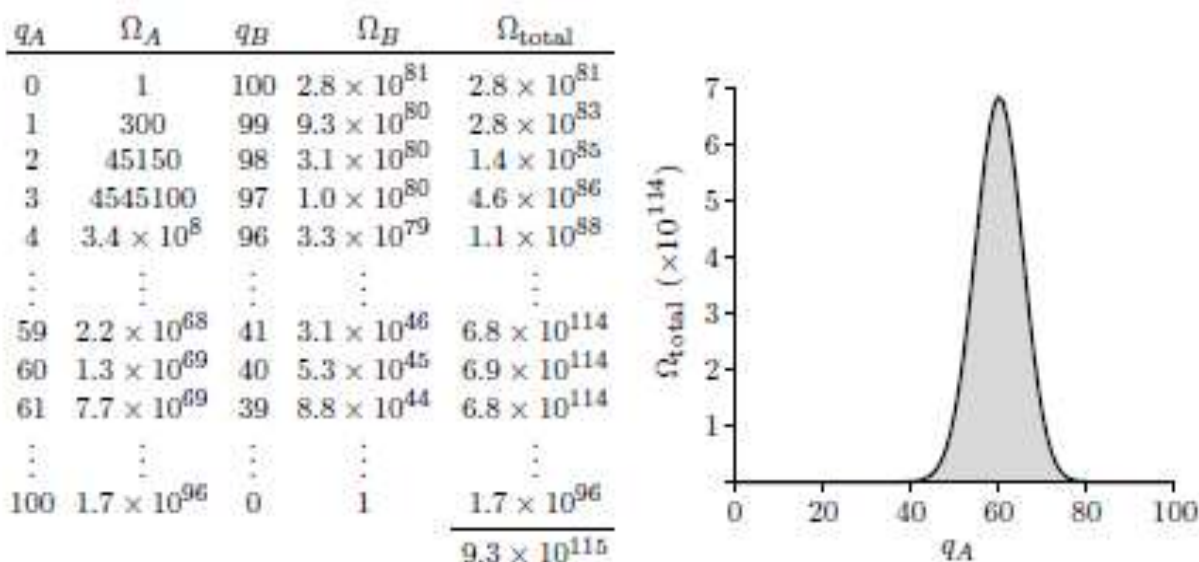| q_A	Ω_A	q_B	Ω_B	Ω_{total}
0	1	100	2.8×10^{81}	2.8×10^{81}
1	300	99	9.3×10^{80}	2.8×10^{83}
2	45150	98	3.1×10^{80}	1.4×10^{85}
3	4545100	97	1.0×10^{80}	4.6×10^{86}
4	3.4×10^8	96	3.3×10^{79}	1.1×10^{88}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
59	2.2×10^{68}	41	3.1×10^{46}	6.8×10^{114}
60	1.3×10^{69}	40	5.3×10^{45}	6.9×10^{114}
61	7.7×10^{69}	39	8.8×10^{44}	6.8×10^{114}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
100	1.7×10^{96}	0	1	1.7×10^{96}
				9.3×10^{115}

Figure 9.8 Macrostates and multiplicities of a system of two Einstein solids, with 300 and 200 oscillators respectively, sharing a total of 100 units of energy

Figure 9.8 shows the table and graph for a system of two Einstein solids with $N_A = 300$, $N_B = 200$, and $q_{total} = 100$. Now there are 101 possible macrostates, of which only a few are shown in the figure. We can see that the least likely macrostate (with all the energy in solid B), has a multiplicity of 3×10^{81}. The most likely macrostate, with $q_A = 60$ has a multiplicity of 7×10^{114}. This means that the most likely macrostate is more than 10^{33} times more probable than the least likely macrostate. Let's examine this system in more detail. The total number of microstates for all the macrostates is 9×10^{115}, so the probability of finding the system in its most likely macrostate is not particularly large ($\approx 7\%$). There are several other macrostates, with q_A slightly smaller or larger than 60, whose probabilities are nearly as large. However, as q_A gets farther away from 60 on either side, the probability drops off very sharply. The probability of finding $q_A < 30$ or $q_A > 90$ is less than one in a million, and the probability of finding $q_A < 10$ is less than 10^{-20}.

Suppose, however, that this system is initially in a state with $q_A \ll 60$, which indicates that virtually all of the energy starts out in solid B. If you wait for the energy to rearrange itself, you are virtually certain to find that energy has flowed from B to A. Thus this system has exhibited **irreversible** behavior. Energy, in the form of heat, has spontaneously flowed from B to A, but never (aside from small fluctuations around $q_A = 60$) from A to B. Thus, heat (and irreversibility) is a *probabilistic* phenomenon due to the statistical properties of thermodynamic systems.

This is a point worth emphasizing since it is contrary to our intuition developed in mechanics. How does the irreversibility of macroscopic phenomena arise? It certainly does not come from the fundamental laws of physics, because these laws are all reversible. One of the

basic principles of classical dynamics is the time-invariance of Newton's laws of motion, which states that the laws of physics are invariant under time reversal. In other words, microscopic phenomena look physically plausible when run in reverse. How can we obtain an irreversible process from the combined effects of a large number of reversible processes? The above example states that while microscopic phenomena are reversible (which is a consequence of the fundamental postulate), macroscopic phenomena are typically *irreversible*. Thus, irreversibility and heat flow are fundamentally probabilistic phenomena. This is consistent with the idea that heat flow is related to changes in the occupation probability distribution as presented in our discussion on the first law from the perspective of the microcanonical ensemble. This can also be explained using the H theorem. For a system far from equilibrium (similar to our example above where $q_A \ll 60$), the H theorem states that H will decrease as the system evolves to equilibrium. However, if we run this process backwards, the system will appear to evolve from equilibrium and the quantity H will correspondingly increase.

With our above example, we have discovered a new way at looking at the 2nd law: The spontaneous flow of energy *stops* when a system is at, or very near, its *most likely macrostate*. In other words, the flow of energy stops when a system is at, or very near, the macrostate with the greatest multiplicity. This law of increasing multiplicity is one version of the second law of thermodynamics. Notice, though, that it's not a *fundamental law* at all (such as Newton's laws), but rather, it's just a very strong statement about probabilities. To make this statement stronger, and to be more realistic in general, we should consider systems with not just a few hundred particles, but more on the order of one mole (10^{23}). To accomplish this, we will examine the multiplicity of an Einstein solid containing a large number of oscillators and energy units. In particular, we will consider the high temperature case where $q \gg N$.

As shown previously, the multiplicity of a large Einstein solid is given by

$$\Omega(N, q) \approx \frac{(q + N)!}{q! \, N!}$$

Taking the natural logarithm and applying Stirling's approximation gives

$$\ln \Omega = \ln(q + N)! \; - \ln q! - \ln N! \approx (q + N) \ln(q + N) - q \ln q - N \ln N$$

We can manipulate the first logarithm above as

$$\ln(q + N) = \ln\left[q\left(1 + \frac{N}{q}\right)\right] = \ln q + \ln\left(1 + \frac{N}{q}\right) \approx \ln q + \frac{N}{q}$$

where the last step follows from the identity $\ln(1+x) \approx x$ for $|x| \ll 1$. Using the above expression allows us to write the multiplicity as

$$\ln \Omega \approx N \ln \left(\frac{q}{N}\right) + N + \frac{N^2}{q} \Rightarrow \Omega(N,q) \approx \exp\left[N \ln \left(\frac{q}{N}\right)\right] = \left(\frac{eq}{N}\right)^N$$

Now for a system of two weakly interacting Einstein solids, the total multiplicity of the combined system, for any given macrostate, is

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

where q_A and q_B are the numbers of energy units in solids A and B. The graph of this expression will have a very sharp peak at $q_A = q/2$, where the energy is distributed equally between the solids. The height of this peak is a very large number:

$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

To determine the sharpness of this multiplicity function, we want to know what the graph looks like *near* this peak. Therefore, we will defined $q_A = q/2 + x$ and $q_B = q/2 - x$, where $x \ll q$. Substituting this into our expression for the multiplicity gives

$$\Omega = \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$

To simplify the second factor, we can take its logarithm and manipulate it to give

$$\ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]^N = N \ln\left[\left(\frac{q}{2}\right)^2 \left(1 - \frac{2x}{q}\right)^2\right] \approx N \left[\ln\left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2\right]^N$$

Substituting this expression into the previous expression gives

$$\Omega = \left(\frac{e}{N}\right)^{2N} \exp\left[N \ln \left(\frac{q}{2}\right)^2\right] \exp\left[-N \left(\frac{2x}{q}\right)^2\right] = \Omega_{max} \exp\left[-N \left(\frac{2x}{q}\right)^2\right]$$

This shows that the multiplicity of two large interacting Einstein solids has a Gaussian form. Because of this, the width of the multiplicity function decreases as $N^{-1/2}$. This result tells us that, when two large Einstein solids are in thermal equilibrium with each other, any random fluctuations away from the most likely macrostate will be *unmeasurable*. To measure such fluctuations we would have to measure the energy to an accuracy of ten significant figures. Once

the system has had time to come to thermal equilibrium, so that all *microstates* are equally probable, it is safe to then assume that it is in its most likely *macrostate*. The limit where a system becomes infinitely large so that measurable fluctuations away from the most likely macrostate never occur is called the **thermodynamic limit**. Thus for interacting Einstein solids, only a tiny fraction of the macrostates of a large interacting system have reasonably large probabilities. This conclusion applies to any pair of interacting objects, provided that the number of particles and the number of energy units are both large.

We have seen from the previous section that particles and energy tend to rearrange themselves until the multiplicity is at (or very near) its maximum value. In fact this conclusion seems to be true for any system provided that it contains enough particles and units of energy for the statistics of very large numbers to apply:

Any large system in equilibrium will be found in the macrostate with the greatest multiplicity (aside from fluctuations that are normally unmeasurable).

This is just a more general statement of the second law of thermodynamics as mentioned earlier.

Let's reiterate the main point in order to present a microscale view of entropy. In the microcanonical ensemble, while all microstates are equally probable, some macrostates are more probable than others. Moreover, note that the total number of microstates accessible to the isolated composite system (i.e. the multiplicity) increases when *any* internal constraint is removed (in the case for the Einstein solid, the internal constraint involved the energy change between the solids). From the microscopic point of view, it's clear that **the multiplicity must either remain the same or increase when an internal constraint is removed**. Hence, in this simple example, we have stumbled on another restatement of the second law of thermodynamics, namely, that for isolated system, the multiplicity tends to increase or remains the same. We will find that as the number of particles in the two subsystems becomes larger (and the energy per particle remains fixed), the probability that energy goes from the hotter to the colder subsystem rapidly increases. In this way, we conclude that it's plausible to identify thermal equilibrium with the most probable macrostate and the entropy with the logarithm of the number of accessible microstates.

Generally, the more particles there are in a system, and the more energy it contains, the greater its multiplicity and its entropy. Besides adding particles and energy, you can increase the entropy of a system by letting it expand into a large space, or breaking large molecules apart into small ones, or mixing together substances that were once separate. In each of these cases, the total number of possible arrangements increases. Since the natural logarithm is a monotonically increasing function of its argument, a macrostate with higher multiplicity also has higher entropy. Therefore, we can restate the second law of thermodynamics in terms of entropy.

Any system in equilibrium will be found in the macrostate with the greatest entropy (aside from fluctuations that are normally too small to measure)

Therefore, an isolated system, being initially in a non-equilibrium state, will evolve from macrostates with lower multiplicity (lower entropy) to macrostates with higher multiplicity (higher entropy). Once the system reaches the macrostates with the highest multiplicity (highest entropy), it will stay there. In this way, **the entropy of an isolated system never decreases**. Notice the similarity between the quantity H and the entropy S in thermodynamics: during any thermodynamic process both are monotonic functions of time. Moreover, equilibrium states *minimize H* and maximize *S*.

9.7 The Third Law

With a microscopic understanding of entropy, we are finally able to discuss the third and final law of thermodynamics. Recall the change of entropy is related to the heat exchanges with a thermodynamic system and its environment:

$$dS = \frac{\delta Q}{T}$$

Since heat and temperature are usually pretty easy to measure, this relation allows us to compute the change in entropy for a wide variety of processes, which has been shown in previous chapters. If the temperature of an object remains constant as heat is added to it (such as during a phase change), then the above expression can be applied even when Q and dS are not infinitesimal. When T is changing, however, it's usually more convenient to write the relation in terms of the heat capacity at constant volume:

$$dS = C_V(T)\frac{dT}{T}$$

This expression can be integrated to give the total change in entropy

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} C_V(T)\frac{dT}{T}$$

Often C_V is fairly constant over the temperature range of interest and thus it can be treated as a constant. However, at low temperature C_V varies as a function of temperature. To compute the system's total entropy, knowledge of C_V must be known down to absolute zero.

$$\Delta S = S_f - S_0 = \int_0^{T_f} C_V(T)\frac{dT}{T}$$

The question now comes of how to calculate S_0. In principle, at zero temperature, a system should settle into its unique lowest-energy state so $\Omega = 1$ and thus $S = 0$. This statement is known as **Planck's statement of the third law of thermodynamics**.

The entropy of every system at zero temperature is zero.

It follows that the entropy of any system in any state, A, can be defined as

$$S_f = \int_0^{T_f} C_V(T)\frac{dT}{T}$$

In practice, however, there can be several reasons why S_0 is effective nonzero. Most importantly, in some solid crystals it is possible to change the orientations of the molecules with very little change in energy. Water molecules, for example, can orient themselves in several possible ways within an ice crystal. Technically, one particular arrangement will always have a lower energy than any other, but in practice the arrangements are often random or nearly random, and you would have to wait for a long time for the crystal to rearrange itself into the true ground state. We then say that the solid has a frozen-in \textbf{residual entropy}. If the ground state has a p-fold degeneracy, then at $T = 0$ there will be p^N available states for the system and the residual entropy will be $S_{res} = Nk \ln p$. An example is carbon monoxide which has a two-fold degenerate ground state, so its residual entropy is $Nk \ln 2$.

Another form of residual entropy comes from the mixing of different nuclear isotopes of an element. Most elements have more than one stable isotope, but in natural systems these isotopes are mixed together randomly with an associated entropy of mixing. Again, at $T = 0$, there should be a unique lowest-energy state in which isotopes are unmixed or are distributed in some orderly way, but in practice the atoms are always stuck at their random sites in the crystal lattice. A third type of residual entropy comes from the multiplicity of alignments spins. At $T = 0$, this entropy does disappear as the spins align parallel or antiparallel to their neighbors.

But this generally doesn't happen until the temperature is less than a tiny fraction of 1 K, far below the range of routine heat capacity measurements.

The third law of thermodynamics was originally postulated by the chemist Walther Nernst and is sometimes referred to as Nernst's "theorem". Although we called the previous statement the Planck statement, it was first proposed by Nernst, who required that:

At $T = 0$, all substance have the same value of entropy.

Planck then recognized that this value could be chosen to be zero. However, this statement is too strong because the ground states of all substance cannot be required to possess the same degeneracy. Thus both statements must be modified and a more appropriate statement of the third law would be:

At $T = 0$, the specific entropy (entropy per particle) is a constant, independent of all the extensive properties of the system.

Consider the implications of the thermodynamic definition of entropy

$$S_f = \int\limits_0^{T_f} C_V(T)\frac{dT}{T}$$

Note that this integral will be undefined at $T = 0$ unless $C_V(T)$ approaches zero "fast enough" as T approaches zero. What is "fast enough"? For the integral to converge, $C_V(T)$ should behave as some positive power of T near absolute zero. Thus, the third law says that the classical theory of heat capacities breaks down at low temperature and requires a more complete theory which yields a $C_V(T) \approx T^\nu$ behavior near $T = 0$, where $\nu > 0$. In other words, for the integral to converge, $C_V \to 0$ as $T \to 0$. This result is also sometimes called the **third law of thermodynamics**

Chapter 10: Classical Statistical Mechanics

We apply the general formalism of statistical mechanics developed in the previous two chapters to systems of many particles and discuss the semiclassical limit of the partition function, the equipartition theorem for classical systems, and the general applicability of the Maxwell velocity distribution. We also will examine various other applications in the semiclassical limit. We will start with a discussion on the canonical ensemble.

10.1 Canonical Ensemble

We have already described the microcanonical ensemble, a collection of isolated systems. Often we are interested in describing systems that interact with other systems. Here we want to describe systems that are in contact with a heat bath or reservoir, able freely to exchange energy by heat with it, but not particles. Just as the members of a microcanonical ensemble are characterized by their internal energy and the number of particles, an ensemble of systems in contact with a heat reservoir is characterized by the temperature of the reservoir and the number of particles and is called a **canonical ensemble**.
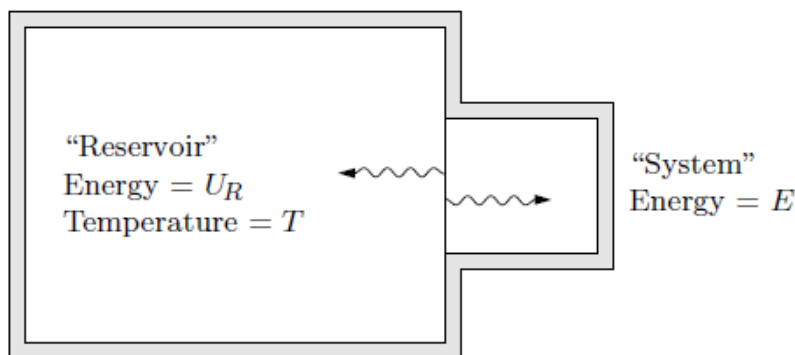
Figure 10.1 A system interacting with a heat reservoir

A heat reservoir is any system that is very large in terms of its number of degrees of freedom compared with the system of interest that is in thermal contact with it. Because the energy of the system is not fixed, we might ask the following question: what is the probability of finding a member of the ensemble in a given state r with energy E_r? To answer this question, consider a system A in equilibrium with a heat reservoir, R, so that the combined system is isolated (therefore a member of the microcanonical ensemble). For any energy E of A, the total number of states available to combined system is

$$\Omega(E) = \Omega_A(E)\Omega_R(E_{total} - E)$$

The *total* number of states available to the system is (as before) the sum over all possible values of the energy of A

$$\Omega(E_{total}) = \sum_{E} \Omega_A(E)\Omega_R(E_{total} - E)$$

Since the combined system belongs to a microcanonical ensemble, the probability of finding our system with energy E is

$$P(E) = \frac{\Omega_A(E)\Omega_R(E_{total} - E)}{\sum_{E_i} \Omega_A(E_i)\Omega_R(E_{total} - E_i)} = C\Omega_A(E)\Omega_R(E_{total} - E)$$

Now since the reservoir is very large compared with our system, $E \ll E_{total}$. So let's expand $\Omega_R(E_{total} - E)$ in a Taylor series about E_{total}. We get

$$ln\, P(E) = ln\, C + ln\, \Omega_R(E_{total}) + ln\, \Omega_A(E) - E\left.\frac{\partial\, ln\, \Omega_R(E')}{\partial E'}\right|_{E'=E_{total}} + \cdots$$

where we have set $E' = E_{total} - E$. Since the temperature of the heat reservoir is

$$\beta = \left(\frac{\partial\, \ln \Omega_R(E')}{\partial E'}\right)_{E'=E_{total}}$$

we could rewrite the probability of finding A with energy E as

$$P(E) = \bar{C}\Omega_A(E)e^{-\beta E}$$

where $\bar{C} = C\Omega_R(E_{total})$ is some constant and $\Omega_A(E)$ is the number of states available to the system A if all we know is that it has energy E. The factor $\Omega_A(E)$ counts the number of states of energy E available to A and is called the **degeneracy** of the energy level E. But now, because the combined system is in the microcanonical ensemble, we can interpret this expression as asserting that the probability of finding A in *any one state, r,* of energy $E = E_r$ is

$$P_r(E_r) = const.\times e^{-\beta E_r}$$

(thus the probability of being in *any* of the states is just above the times the number of states of the same energy). The constant is to be determined by normalization, i.e.,

$$\sum_r P_r = const. \times \sum_r e^{-\beta E_r} = 1$$

If we define the constant as $1/Z$, then for any state r, the probability is given by

$$P_r(E_r) = \frac{1}{Z}\exp[-\beta E_r] \quad (10.1)$$

This is the **Boltzmann distribution** and it characterizes the **canonical ensemble**. Notice that nothing has been said about A except that it must be small relative to R and that it must be in thermal equilibrium with it. This is required only to ensure that A is at a fixed temperature. Thus, we could, for example, take A to be a single microscopic component of R itself. For example, we could take A to be a single molecule of a gas at a fixed temperature, T, so that the rest of the gas then acts as the heat reservoir. Then the probability of finding the molecule with energy U is given precisely by Equation (10.1). Suppose that the ground state energy of our atom is $E_0 = 0$, while the excited states all have positive energies. According to the Boltzmann distribution, the probability of the ground state is $1/Z$ and all other states have smaller probabilities proportional to the temperature.

Example 1: Thermal Excitation of Atoms

Consider a hydrogen atom in the atmosphere of the sun where the temperature is about 5800 K. What is the probability of finding the atom in one of its first excited states (s_2) compared to the probability of finding it in the ground state (s_1)?

We can determine this by examining the ratio of the probabilities
$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = \exp\left[-\frac{(E_2 - E_1)}{kT}\right]$$
Note that the ratio of probability is equal to a ratio of simple exponential factors, each of which is a function of the energy of the corresponding microstate and the temperature of the reservoir. Each of these exponential factors is called a **Boltzmann factor**. Based on quantum mechanics, the difference in energy between the ground state and the first excited state is 10.2 eV. Thus, for a hydrogen atom in the atmosphere of the sun, the ratio of probabilities is approximately 1.4×10^{-9}. This implies that for every billion atoms in the ground state, roughly 1.4 (on average) will be in any one of the first excited states.

Atoms in the atmosphere of the sun can absorb sunlight on its way toward earth, but only at wavelengths that can induce transitions of the atoms into higher excited states. A hydrogen atom in its first excited state can absorb wavelengths in the Balmer series. Since the Balmer lines are more prominent among the other gases in the solar atmosphere (i.e. iron, magnesium, sodium, etc.), then it can be shown that hydrogen atoms are much more abundant in the sun's atmosphere than any of these other types.

Example 2: Cold Interstellar Molecular Clouds

Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational excited states have an energy of $4.7 \times 10^{-4}\ eV$ (above the ground state). There are actually three such excited states, all with the same energy. Studies of the absorption spectrum of starlight that passes through these molecular clouds showed that for every ten CN molecules that are in the ground state, approximately three others are in the three first excited states. Thus, astronomers have suggested that the molecules might be in thermal equilibrium with a well-defined temperature "reservoir". What is the temperature of the reservoir?

If the molecules are in equilibrium with a reservoir of temperature T, then the probability of a molecule being in any one of the excited states, relative to the ground state, should be

$$\frac{P(s_1)}{P(s_0)} = \frac{e^{-E_1\ /kT}}{e^{-E_0\ /kT}} = \exp\left[-\frac{(E_1 - E_0)}{kT}\right]$$

We are given that this relative probability is approximately 1/10. Therefore

$$-\frac{(E_1 - E_0)}{kT} = \ln\frac{1}{10} = -2.303 \Rightarrow T = 2.4\ K$$

Thus the interstellar clouds are likely in thermal equilibrium with the cosmic microwave background.

10.2 Partition Function

Given any distribution, we can calculate the average values of interesting quantities as explained earlier. Let the quantity X take the value X_r in state r, then the average value of X for a classical system is given by the phase-space integral

$$\langle X \rangle = \frac{\int \prod_i d^3\vec{r}_i\ \prod_i d^3\vec{p}_i\ \rho(\vec{r}_i, \vec{p}_i) X(\vec{r}_i, \vec{p}_i)}{\int \prod_i d^3\vec{r}_i\ \prod_i d^3\vec{p}_i}$$

over all accessible values of $\vec{r}$ and $\vec{p}$ for each particle of the system A. $\rho(\vec{r}_i, \vec{p}_i)$ is the probability density function,

$$\rho(\vec{r}_i, \vec{p}_i) = \Omega\big(U(\vec{r}_i, \vec{p}_i)\big)e^{-\beta U(\vec{r}_i, \vec{p}_i)}$$

which is a function of the internal energy of A.

Fortunately, there is a more direct way to perform calculations in the canonical ensemble. First, we need to normalize the Boltzmann function. To normalize the Boltzmann distribution, we need to determine Z, using the assumption that the total probability must be 1

$$1 = \sum_s P(s) = \sum_s \frac{1}{Z}\exp[-\beta E_s]$$

$$Z = \sum_s e^{-\beta E(s)} \rightarrow \frac{1}{h_o{}^3}\int d^3\vec{r}\, d^3\vec{p}\; e^{-\beta E(p,r)}$$

The quantity Z is called the **partition function** and it is the sum of all Boltzmann factors. The partition function essentially counts how many states are accessible to the system, weighting each one in proportional to its probability. The partition function does not depend explicitly on the energy but on the temperature. It plays a role analogous to that of the multiplicity in the microcanonical ensemble and, as we will now show, all the thermodynamic functions can be expressed directly it terms of it and its derivatives, so that a knowledge of the partition function is sufficient for a complete treatment of systems in the canonical ensemble.

10.2.1 Thermodynamics in Canonical Ensemble

First, let's determine the internal energy within the canonical ensemble.

$$\langle U \rangle = \sum_r P_r U_r = \frac{\sum_r U_r e^{-\beta U_r}}{\sum_r e^{-\beta U_r}} = \frac{1}{Z}\sum_r U_r e^{-\beta U_r} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

The generalized forces are

$$\langle F_\alpha \rangle = \sum_r F_\alpha P_r = -\frac{\sum_r \left(\frac{\partial U_r}{\partial X_\alpha}\right)e^{-\beta U_r}}{\sum_r e^{-\beta U_r}} = -\frac{1}{Z}\sum_r \left(\frac{\partial U_r}{\partial X_\alpha}\right)e^{-\beta U_r} = \frac{1}{Z}\frac{\partial}{\partial X_\alpha}\left(\sum_r e^{-\beta U_r}\right) = \frac{1}{Z}\frac{\partial Z}{\partial X_\alpha}$$

$$= \frac{\partial \ln Z}{\partial X_\alpha}$$

From these, we also derive an expression for the entropy as follows. Consider an isothermal quasi-static process in which the partition function undergoes a change dZ. Notice that $Z = Z(\beta, X_\alpha)$ and one has

$$d \ln Z = \frac{\partial \ln Z}{\partial \beta} d\beta + \sum_\alpha \frac{\partial \ln Z}{\partial X_\alpha} dX_\alpha = -\langle U \rangle d\beta + \beta \sum_\alpha \langle F_\alpha \rangle dX_\alpha$$

$$= -d(\beta \langle U \rangle) + \beta d\langle U \rangle - \beta \sum_\alpha \delta W_\alpha$$

Rearranging the above expression gives

$$\beta^{-1} d(\ln Z + \beta \langle U \rangle) = d\langle U \rangle - \sum_\alpha \delta W_\alpha$$

\noindent which, comparing the above expression with the first law of thermodynamics, means that the left hand side must be associated with the entropy. Therefore,

$$T \, dS = \beta^{-1} d(\ln Z + \beta \langle U \rangle) \Rightarrow S = k(\ln Z + \beta \langle U \rangle)$$

How does this definition of entropy compare to the Boltzmann-Gibbs entropy that we saw last chapter? To see that it reduces to the definition, we saw last chapter, we notice that in the canonical ensemble the normalized probability has the form

$$P_r = \frac{e^{-\beta U_r}}{\sum_s e^{-\beta U_s}} = \frac{1}{Z} e^{-\beta U_r} \Rightarrow \ln P_r = -\beta U_r - \ln Z$$

which, when substituted into the expression for the Boltzmann-Gibbs entropy, gives

$$S_{Gibbs} = -k \sum_r \frac{e^{-\beta U_r}}{Z} [\beta U_r - \ln Z] = k [\ln Z + \beta \langle U \rangle]$$

as we expected. We see that indeed the Gibbs definition is more general, under appropriate conditions giving the expressions in the microcanonical ensemble and in the canonical ensemble.

The other thermodynamic functions also have expressions in terms of Z and its derivatives. It turns out that the most useful and important thermodynamic potential in the canonical ensemble is the Helmholtz free energy

$$F = U - TS = \langle U \rangle - kT(\ln Z + \beta \langle U \rangle) = \langle U \rangle - \frac{1}{\beta}(\ln Z + \beta \langle U \rangle) = -\frac{1}{\beta} \ln Z$$

Just as the partition function plays the same role in canonical ensemble as the multiplicity function plays in microcanonical ensemble, the Helmholtz free energy plays the same role in the canonical ensemble as the entropy in the microcanonical ensemble. This should not be a surprising result.

Consider a thermally isolated system. If the volume is fixed, then no work is done and thus the internal energy of the system is conserved. While this constraint is always in place, the system might be out of equilibrium (e.g. we move a piston that separates two sub-systems). If the system is initially out of equilibrium, then some **spontaneous processes will drive the system towards equilibrium**. In a state of stable equilibrium, no further spontaneous, no further spontaneous processes (other than ever-present random fluctuations) can take place. All equilibrium state corresponds to the maximum multiplicity and maximum entropy. All microstates in equilibrium are equally accessible (the system is in one of these microstates with equal probability). This implies that in any of these spontaneous processes, the entropy tends to increase, and the change entropy satisfies the condition $dS \geq 0$. Suppose we place this system in contact with a thermal reservoir, there are now two complications:

1. The energy in the system is no longer fixed (it may flow between the system and reservoir)
2. In order to investigate the stability of an equilibrium position, we need to consider the entropy of the combined system – according to the second law the total entropy should be maximized.

From our discussion on free energy, the system should minimize its free energy in order to maximize the total entropy of the combined system. Since volume is usually the external parameter of the system, it is usually the Helmholtz free energy that determines the system's behavior when connected to a heat reservoir. Thus, the Helmholtz free energy should dictate the evolution of the system. Moreover, since $F(T,V)$ is a fundamental surface, then all other thermodynamic quantities can be derived from it. In particular, the usefulness of $F = -kT \ln Z$ is that from F, we can compute the entropy, pressure, and chemical potential

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

There is one other useful property of the partition function that allows us to analyze various thermodynamic systems. Consider a system C consisting of two parts, A and B, which do not interact, or interact weakly but are in contact with the same heat reservoir at inverse temperature β. The microstates of the combined system will be labeled by the pair (r, s) where r is a state of A and s is a state of B. Let A be in state r and B in state s, so that the energy of combined system is $U_{rs} = U_r + U_s$ as there is no interaction between A and B. The partition function for the combined system is therefore

$$Z_{total} = \sum_{r,s} e^{-\beta(U_r+U_s)} = \sum_r e^{-\beta U_r} \sum_s e^{-\beta U_s} = Z_A Z_B$$

By induction, we may generalize the above result to a combined system consisting of N subsystems none of which interact. We will have

$$Z_{total} = \prod_{j=1}^{j=N} Z_j$$

which is the powerful result that the partition function of a system consisting of N non-interacting sub-systems is just the product over all partition functions of the individual sub-systems. It is easy to see now that the average energy is extensive, i.e., the average energy of a composite system will just be the sum over the average energies of each sub-system

$$\langle U \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \sum_{j=1}^{N} \ln Z_j = \sum_{j=1}^{N} \langle U_j \rangle$$

where we have made use of the properties of the logarithm. Indeed, because the logarithm of a product is the sum of logarithms, we see immediately that the following variables are extensive: the mean energy, the entropy and all the thermodynamic potentials.

With the knowledge of the partition function, we now have a basic procedure in which we can bridge the gap between the statistical mechanics of the canonical ensemble and thermodynamics. The basic procedure is as follows

1. Define the microstates for the given thermodynamic systems and determine the energy of the microstates.
2. Find $Z(U, N, X_\alpha)$ for the given thermodynamic system
3. Evaluate the Helmholtz free energy using

$$F(T, V, N) = -\frac{1}{\beta} \ln Z$$

4. Evaluate the entropy of the system using

$$S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

5. Evaluate the internal energy of the system using

$$U(T, V, N) = F(T, V, N) + TS(T, V, N)$$

Example 3: Einstein solid

Consider an Einstein solid in thermal contact with a heat reservoir at a temperature T. Based on our previous discussion on the Einstein solid, the energy for a quantum harmonic oscillator is given by $E_n = (n + 1/2)\hbar\omega$. To analyze the thermal behavior of the Einstein solid, we have to determine the partition function. The partition function is given by

$$Z = \exp\left[-\frac{\beta\hbar\omega}{2}\right] \sum_{n=0}^{\infty} \exp[-\beta n\hbar\omega] = \exp\left[-\frac{\beta\hbar\omega}{2}\right] \sum_{n=0}^{\infty} \exp[-\beta\hbar\omega]^n$$

We note that the sum is an infinite geometric series in $\exp[-\beta\hbar\omega]$ so it can be directly evaluated to find

$$Z = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

For an Einstein solid of N oscillators we have

$$Z_N = \prod_{j=1}^{N} Z_j = \frac{1}{2^N \sinh^N(\beta\hbar\omega/2)}$$

The average energy of the Einstein solid is given by

$$\langle U \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[-N \ln\left(\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)\right] = \frac{N\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

which is the same as in the microcanonical ensemble.

Example 4: Spin-1/2 Paramagnet

Consider a system of charged, weakly interacting spin ½ particles that is kept in contact with a heat reservoir at a fixed temperature T and placed in an external magnetic field $\vec{B}$. Due to the presence of the field, the particles will tend to align themselves with the field in order to reduce the total energy of the system

$$U = -\vec{M} \cdot \vec{B} = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow)$$

To analyze the thermal behavior of this system, we have to determine the partition function. According to the Boltzmann distribution, the probabilities of finding a single aligned or anti-aligned particle are

$$P(E_+) = \frac{1}{Z} e^{-\beta \mu B} \qquad P(E_-) = \frac{1}{Z} e^{\beta \mu B}$$

The partition function is given by

$$Z = \sum_r e^{-\beta E_r} = e^{-\beta \mu B} + e^{\beta \mu B} = 2 \cosh(\beta \mu B)$$

For a system of N non-interacting magnetic moments, we have

$$Z_N = \prod_{j=1}^{N} Z_j = 2^N \cosh^2(\beta \mu B)$$

The average energy of each particle is

$$\langle U \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\mu B \beta \tanh(\mu B \beta)$$

just as in the microcanonical ensemble.

Example 5: Monatomic Ideal Gas

Consider N non-interacting particle within a box (i.e. an ideal gas). For an ideal gas, the energy is purely kinetic and thus is given by $E = p^2/2m$. To evaluate the partition function, we need to use the continuum approximation. Thus, the partition function of the monatomic ideal gas is given by

$$Z = \frac{1}{h_o^3} \int d^3\vec{r}\, d^3\vec{p}\ e^{-\beta E(p,r)} = \frac{V}{h_o^3} \left(\int_{-\infty}^{\infty} dp\, e^{-\frac{\beta p^2}{2m}} \right)^3 = \frac{V}{h_o^3} \left(\sqrt{\frac{\pi}{\frac{\beta}{2m}}} \right)^3 = V \left(\frac{2\pi m}{\beta h_o^2} \right)^{3/2}$$

For a classical ideal gas of N particles, we have

$$Z_N = \prod_{j=1}^{N} Z_j = V^N \left(\frac{2\pi m}{\beta h_o^2} \right)^{3N/2}$$

The average energy of a molecule is given by

$$\langle U \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta} \left[N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi m}{h_o^2} \right) - \frac{3N}{2} \ln \beta \right] = \frac{3N}{2\beta} = \frac{3}{2} NkT$$

The entropy of a molecule is given by

$$S = k(\ln Z + \beta \langle U \rangle) = Nk \left(\ln \left[V \left(\frac{2\pi m}{\beta h_o{}^2} \right)^{3/2} \right] + \frac{3}{2} \right)$$

We should note here that the entropy result derived here is *not* the same as that derived for the microcanonical ensemble. We will perform this calculation more closely in the next section.

10.3 The Ideal Gas in the Semiclassical Limit

Let's apply the canonical ensemble to an ideal gas in the semiclassical limit. Because the thermodynamic properties of a system are independent of the choice of ensemble, we will find the same thermal and pressure equations of state as we found in the microcanonical ensemble. Although we will not obtain any new results, this application will give us more experience in working with the canonical ensemble and again show the subtle nature of the semiclassical limit. In the next chapter, we will derive the classical equations of state using the grand canonical ensemble without any ad hoc assumptions. Suppose that a gas is in thermal equilibrium with a heat bath at temperature T. Therefore, it is more natural and convenient to treat the ideal gas in the canonical ensemble than in the microcanonical ensemble. Because the particles are not localized, they cannot be distinguished from each other. Hence, we cannot simply focus our attention on one particular particle. The approach we will take here is to treat the particles as distinguishable, and then correct for the error approximately.

Let's consider a system of noninteracting particles starting from their fundamental description according to quantum mechanics. If the temperature is sufficiently high, we expect that we can treat the particles classically. To do so, we cannot simply take the limit $\hbar \to 0$ wherever it appears because the counting of microstates is different in quantum mechanics and classical mechanics. That is, particles of the same type are indistinguishable according to quantum mechanics. So in the following we will consider the semiclassical limit, and the particles will remain indistinguishable even in the limit of high temperatures.

To take the semiclassical limit, the mean de Broglie wavelength $\bar{\lambda}$ of the particles must be smaller than any other length in the system. For an ideal gas the only two lengths are L, the linear dimension of the system, and the mean distance between particles. Because we are interested in the thermodynamic limit for which $L \gg \bar{\lambda}$, the first condition will always be satisfied. Since the mean distance between particles in three dimensions is $\rho^{-1/3}$, the semiclassical limit requires that $\bar{\lambda} \ll \rho^{-1/3}$. The calculation of the partition function of an ideal gas in the semiclassical limit proceeds as follows. First, we assume that $\bar{\lambda} \ll \rho^{-1/3}$ so that we can pick out one particle if we make the additional assumption that the particles are distinguishable (because we will have to correct for the latter assumption later).

With these considerations in mind, we now calculate Z_1, the partition function for one particle in the semiclassical limit. Consider the microstates of a single classical particle of mass m confined to a one-dimensional box of length L. We know that the microstate is specified by its position x and momentum p. Because the values of the position and momenta of a particle are continuous variables, the number of microstates of the system with energy U is not meaningful and instead we will determine the quantity $g(E)\Delta E$, the number of microstates between E and $E + \Delta E$. The quantity $g(E)$ is called the **density of states**. However, it's easier to first calculate Ω_E, the number of microstates of the system with energy less than or equal to E. The number of microstates between E and $E + \Delta E$, is related to Ω_E by

$$g(E)\Delta E = \Omega(E + \Delta E) - \Omega(E) \approx \frac{d\Omega(E)}{dE} dE$$
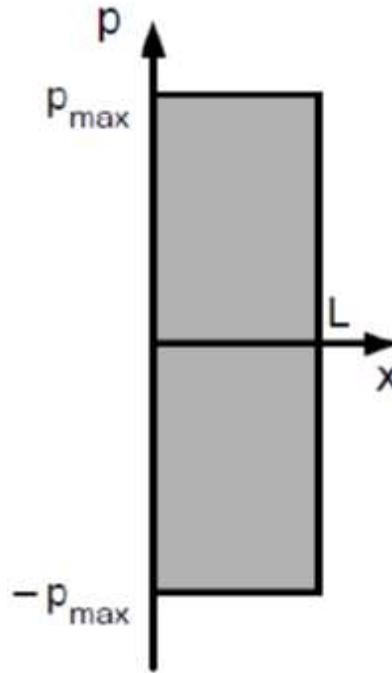
Figure 10.2 The phase space of a single particle of mass m with energy less than or equal to E in a 1D box of length L

If the energy of the particle is E and the dimension of the box is L, then the microstates of the particle with energy less than or equal to E are restricted to the rectangle shown in Figure 10.2, where $p_{max} = \sqrt{2mE}$. Because the possible values of x and p are continuous, there are an infinite number of microstates within the rectangle. The area of the phase space occupied by the trajectory of a particle whose position $x \leq L$ and whose energy is less than or equal to E is equal to $2p_{max}L$. Therefore, the number of cells or microstates equals

$$\Omega_{cl}(E) = \frac{2p_{max}L}{\Delta x \Delta p} = 2\frac{L}{\Delta x \Delta p}\sqrt{2mE}$$

In classical physics, there is no criterion for choosing the values of Δx and Δp. What is the corresponding density of states? Quantum theory requires that the area $\Delta x \Delta p$ of a cell in phase space is given by $\Delta x \Delta p = h$. Thus, Planck's constant h can be interpreted as the minimum area of a cell in a two-dimensional phase space. That is, in order for the counting of microstates in a classical system to be consistent with the more fundamental counting of microstates in a quantum system, we cannot specify a microstate of the classical system more precisely than to assign it to a cell of area h in phase space. This fundamental limitation implies that the subdivision of phase space into cells of area less than h is physically meaningless, a result consistent with the Heisenberg uncertainty principle.

Quantum theory also states that a single particle of mass m in a one-dimensional box of length L has wave properties associated with it, and the corresponding wave has a node at the boundaries of the box. This implies that the linear momentum of a particle can be written in terms of the wavenumber (a result given by de Broglie) as $p = \hbar k = \hbar(\pi/L)n$. The energy of the particle is given by

$$E = \frac{1}{2m}\left(p_x^2 + p_y^2\right)$$

In two dimensions the wave number becomes a wave vector $\vec{k}$, which satisfies the one-dimensional condition in each direction

$$k_x = \frac{\pi}{L_x}n_x, \quad k_y = \frac{\pi}{L_y}n_y$$

The corresponding energy eigenvalues are given by

$$E_{n_x,n_y} = \frac{h^2}{2m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$

The generalization to three dimensions is straightforward. If we assume that the box is a cube with linear dimension L, the energy eigenvalues of a particle are

$$\epsilon_n = \frac{h^2}{8mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$

where the subscript n represents the set of quantum numbers n_x, n_y, and n_z, each of which can be any nonzero, positive integer. The corresponding partition function is given by

$$Z_1 = \sum_n e^{-\beta \epsilon_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2(n_x^2+n_y^2+n_z^2)/8mL^2}$$

$$= \left(\sum_{n_x=1}^{\infty} e^{-\beta h^2 n_x^2/8mL^2} \right) \left(\sum_{n_y=1}^{\infty} e^{-\beta h^2 n_y^2/8mL^2} \right) \left(\sum_{n_z=1}^{\infty} e^{-\beta h^2 n_z^2/8mL^2} \right)$$

$$= \left(\sum_{n_i=1}^{\infty} e^{-\alpha^2 n_i^2} \right)^3$$

where $\alpha = \beta h^2/8mL^2$. It remains to evaluate the sum in the expression above. Because the linear dimension L of the container is of macroscopic size, we have $\lambda \ll L$ and $\alpha \ll 1$. Hence, because the difference between successive terms in the sum is very small, we can convert the sum to an integral

$$Z_1 = \left(\sum_{n_i=1}^{\infty} e^{-\alpha^2 n_i^2} \right)^3 = \left(\sum_{n_i=0}^{\infty} e^{-\alpha^2 n_i^2} - 1 \right)^3 \rightarrow \left(\int_0^{\infty} e^{-\alpha^2 n_i^2} dn_i - 1 \right)^3$$

Evaluating the integral using a change of variables $u^2 = -\alpha^2 n_i^2$, we have

$$Z_1 = \left(\frac{1}{\alpha} \int_0^{\infty} e^{-u^2} du - 1 \right)^3 = \left(L \left(\frac{2\pi m}{\beta h^2} \right)^{1/2} - 1 \right)^3 \approx V \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}}$$

The result is the partition function associated with the translational motion of one particle in a box.

It is straightforward to find the mean pressure and energy for one particle in a box. We take the logarithm of both sides of Z_1 and find that

$$\ln Z_1 = \ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right)$$

The mean pressure due to one particle is given by

$$\langle P \rangle = \frac{1}{\beta} \left(\frac{\partial \ln Z_1}{\partial V} \right)_{T,N} = \frac{1}{\beta V} = \frac{kT}{V}$$

and the mean energy is

$$\langle U \rangle = -\left(\frac{\partial \ln Z_1}{\partial \beta}\right)_{V,N} = \frac{3}{2\beta} = \frac{3}{2}kT$$

The mean energy and pressure of an ideal gas of N particles is N times that of the corresponding quantities for one particle. Hence, we obtain for an ideal classical gas, the equations of state:

$$\langle P \rangle = \frac{NkT}{V}, \quad \langle U \rangle = \frac{3}{2}NkT$$

The heat capacity at constant volume of an ideal gas of N particle is

$$C_V = \left(\frac{\partial \langle U \rangle}{\partial T}\right)_V = \frac{3}{2}Nk$$

We have derived the mechanical and thermal equations of state for an ideal classical gas for a second time. The derivation of the equations of state is much easier in the canonical ensemble than in the microcanonical ensemble. The reason is that we were able to consider the partition function of one particle because the only constraint is that the temperature is fixed instead of the total energy.

Although it is straightforward to calculate the mean energy and pressure of an ideal classical gas by considering the partition function for one particle, the calculation of the entropy is more subtle. To understand the difficulty, consider the calculation of the partition function of an ideal gas of two particles. Because there are no interactions between the particles, we can write the total energy as a sum of the single particle energies $\epsilon_1 + \epsilon_2$, where ϵ_i is the energy of the ith particle. The partition function Z_2 is

$$Z_2 = \sum_{all\ states} e^{-\beta(\epsilon_1+\epsilon_2)}$$

The sum over all microstates is over the microstates of the two-particle system. If the two particles were distinguishable, there would be no restriction on the number of particles that could be in any single particle microstate, and we could sum over the possible microstates of each particle separately. Hence, the partition function for a system of two distinguishable particles has the form: $Z_{2,distinguishable} = Z_1^2$.

It's instructive to show the origin of the above relation for a specific example. Suppose the two particles are red and blue and are in equilibrium with a heat bath at temperature T. For simplicity, we assume that each particle can be in one of three microstates with energies ϵ_a, ϵ_b, and ϵ_c. The partition function for one particle is given by

$$Z_1 = e^{-\beta\epsilon_a} + e^{-\beta\epsilon_b} + e^{-\beta\epsilon_c}$$

It can be shown that there are 9 possible microstates of this system of two distinguishable particles. The corresponding partition function is given by

$$Z_{2,distinguishable} = e^{-2\beta\epsilon_a} + e^{-2\beta\epsilon_b} + e^{-2\beta\epsilon_c} + 2\left[e^{-\beta(\epsilon_a+\epsilon_b)} + e^{-\beta(\epsilon_a+\epsilon_c)} + e^{-\beta(\epsilon_b+\epsilon_c)}\right] = Z_1^2$$

In contrast, if the two particles are indistinguishable, many of the possible microstaes cannot be counted as separate microstates. In this case we cannot assign the microstates of the particles independently, and the sum over all microstates. As stated earlier, the semiclassical limit assumes that microstates with multiple occupancy such as *a,a* and *b,b* can be ignored because there are many more single particle states than there are particles. (In our simple example, each particle can be in one of only three microstates, and the number of microstates is comparable to the number of particles.) If we assume that the particles are indistinguishable and that microstates with multiple occupancy can be ignored, then Z_2 is given by

$$Z_{2,indistinguishable} = e^{-\beta(\epsilon_a+\epsilon_b)} + e^{-\beta(\epsilon_a+\epsilon_c)} + e^{-\beta(\epsilon_b+\epsilon_c)}$$

We see that if we ignore multiple occupancy there are three microstates for indistinguishable particles and six microstates for distinguishable particles. Hence, in the semiclassical limit, we can write $Z_2 = Z_1^2/2!$ where the factor of 2! corrects for overcounting. For three particles (each of which can be in one of three possible microstates) and no multiple occupancy, there would be one microstate of the system for indistinguishable particles and no multiple occupancy, namely, the microstate a, b, c. However, there would be six such microstates for distinguishable particles. Thus, if we count microstates assuming that the particles are distinguishable, we would overcount the number of microstates by $N!$, the number of permutations of N particles.

We conclude that if we begin with the fundamental quantum mechanical description of matter, then identical particles are indistinguishable at all temperatures. If we make the assumption that single particle microstates with multiple occupancy can be ignored, we can express the partition function of N noninteracting identical particles as

$$Z_N = \frac{Z_1^N}{N!} \Rightarrow Z_N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

If we take the logarithm of both sides of the above equation and use Stirling's approximation, we can write the Helmholtz free energy of an ideal classical gas as

$$F = -kT \ln Z_N = -NkT \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + 1\right]$$

The entropy can be found from the relations $F = U - TS$ or $S = -\partial F/\partial T$, giving

$$S(T,V,N) = Nk \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]$$

This form of S is known as the **Sackur-Tetrode equation**, which is the same form of the entropy derived in the microcanonical ensemble. Rewriting $U = (3/2)NkT$ for an ideal classical gas enables us to rewrite the entropy as

$$S(U,V,N) = Nk \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mU}{3Nh^2}\right) + \frac{5}{2}\right]$$

10.4 Kinetic Theory

From our discussions of the ideal gas in the semiclassical limit, we found that the approach to the classical limit must be made with care. Planck's constant appears in the expression for the entropy even for the simple case of an ideal gas, and the indistinguishability of the particles is not a classical concept. If we work entirely within the framework of classical mechanics, we would replace the sum over microstates in the partition function by an integral over phase space, that is,

$$Z_{N,classical} = C_N \int e^{-\beta U(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N,\vec{p}_1,\vec{p}_2,\dots,\vec{p}_N)} d\vec{r}_1 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N$$

The constant C_N cannot be determined from classical mechanics. From our counting of microstates for a single particle, we see that we can obtain results consistent with starting from quantum mechanics if we choose the constant C_N to be

$$C_N = \frac{1}{N!\, h^{3N}}$$

Thus the partition function of a system of N particles in the semiclassical limit can be written as

$$Z_{N,classical} = \frac{1}{N! \, h^{3N}} \int e^{-\beta U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, \vec{p}_1, \vec{p}_2, ..., \vec{p}_N)} d\vec{r}_1 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N$$

In the following subsections, we integrate $Z_{N,classical}$ over phase space in order to find some general properties of classical systems of many particles.

10.4.1 The Equipartition Theorem

We have used the canonical ensembles to show that the energy of an ideal classical gas in three dimensions is given by $U = (3/2)NkT$. This is a special case of the \textbf{equipartition theorem** which can be stated as follows:

For a classical system in equilibrium with a heat bath at temperature T, the mean value of each contribution to the total energy that is quadratic in a coordinate equals $kT/2$.

Note that the equipartition theorem holds regardless of the coefficients of the quadratic terms and is valid only for a classical system. If all the contributions to the energy are quadratic, the mean energy is distributed equally to each term (hence the "equipartition"). To see how to calculate averages according to classical statistical mechanics, we first consider a single particle subject to a potential energy $U_{pot}(r)$ in equilibrium with a heat bath at temperature T. Classically, the probability of finding the particle in a small volume $d\vec{r}$ about $\vec{r}$ with a momentum in a small volume $d\vec{p}$ about $\vec{p}$ is proportional to the Boltzmann factor and the volume $d\vec{r} d\vec{p}$ in phase space:

$$P(\vec{r}, \vec{p}) = A \exp\left[-\beta\left(\frac{p^2}{2m} + U_{pot}(\vec{r})\right)\right] d\vec{r} d\vec{p}$$

To normalize the probability and determine the constant A we have to integrate over all the possible values of r and p.

We next consider a classical system of N particles in the canonical ensemble. The probability density of a particular microstate is proportional to the Boltzmann probability $e^{-\beta U}$, where U is the energy of the microstate. Because a microstate is defined classically by the positions and momenta of every particle, we can express the average of any physical quantity $f(r, p)$ in a classical system as

$$\langle X \rangle = \frac{\int \prod_i d^3\vec{r}_i \ \prod_i d^3\vec{p}_i \ e^{-\beta U(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,\vec{p}_1,\vec{p}_2,...,\vec{p}_N)} X(\vec{r}_i,\vec{p}_i)}{\int \prod_i d^3\vec{r}_i \ \prod_i d^3\vec{p}_i \ e^{-\beta U(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,\vec{p}_1,\vec{p}_2,...,\vec{p}_N)}}$$

Note that the sum over quantum states has been replaced by an integration over phase space. We could divide the numerator and denominator by h^{3N} so that we would obtain the correct number of microstates in the semiclassical limit, but this factor cancels in calculations of average quantities. We have already seen that the mean energy and mean pressure do not depend on whether the factors of h^{3N} and $1/N!$ are included in the partition function.

Suppose that the total energy can be written as a sum of quadratic terms. For example, the kinetic energy of one particle in three dimensions in the nonrelativistic limit can be expressed as $\left(p_x^2 + p_y^2 + p_z^2\right)/2m$. For simplicity, let's consider a one-dimensional system of two particles, and suppose that the energy of the system can be written as

$$U = \epsilon_1(p_1) + \tilde{U}(x_1, x_2, p_2)$$

where $\epsilon_1 = ap_1^2$ with a equal to a constant. We have separated out the quadratic dependence of the energy of particle one on its momentum. The mean value of ϵ_1 as

$$\langle \epsilon_1 \rangle = \frac{\int \prod_i d^3\vec{r}_i \ \prod_i d^3\vec{p}_i \ e^{-\beta U_i} \epsilon_1}{\int \prod_i d^3\vec{r}_i \ \prod_i d^3\vec{p}_i \ e^{-\beta U_i}} = \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta \epsilon_1} dp_1 \int_{-\infty}^{\infty} e^{-\beta \tilde{U}} dx_1 dx_2 dp_2}{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta \epsilon_1} dp_1 \int_{-\infty}^{\infty} e^{-\beta \tilde{U}} dx_1 dx_2 dp_2} = \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta \epsilon_1} dp_1}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1}$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \right) = -\frac{\partial}{\partial \beta} \ln \frac{\pi}{\beta a} = \frac{1}{2} kT$$

This is an example of the equipartition theorem of classical statistical mechanics. The equipartition theorem is applicable only when the system can be described classically, and is applicable only to each term in the energy that is proportional to a coordinate squared. This coordinate must take on a continuum of values from $-\infty$ to ∞. The equipartition theorem is valid only in classical statistical mechanics, which is an excellent approximation as long as $\Delta E \ll kT$. In most quantum systems the spacing between successive energy levels decreases with increasing energy and the equipartition theorem becomes a good approximation at high temperatures. On the other hand, the spacing between the energy levels lying close to the ground state can be large and equipartition will fail at low temperatures as a consequence.

A system of particles in three dimensions has *3N* quadratic contributions to the kinetic energy, three for each particle. From the equipartition theorem, we know that the mean kinetic energy is $(3/2)NkT$, independent of the nature of the interactions, if any, between the particles.

Hence, the heat capacity at constant volume of an ideal classical monatomic gas is given by $C_V = (3/2)Nk$ as we have found previously.

Another application of the equipartition function is to the one-dimensional harmonic oscillator in the classical limit. In this case there are two quadratic contributions to the total energy and hence the mean energy of a one-dimensional classical harmonic oscillator in equilibrium with a heat bath at temperature T is kT. In the harmonic model of a crystal each atom feels a harmonic or spring-like force due to its neighboring atoms. The N atoms independently perform simple harmonic oscillations about their equilibrium positions. Each atom contributes three quadratic terms to the kinetic energy and three quadratic terms to the potential energy. Hence, in the high temperature limit the energy of a crystal of N atoms is $U = 3NkT$, and the heat capacity at constant volume is $C_V = 3Nk$. The result is known as the **law of Dulong and Petit**, as discussed previously. This result was first discovered empirically and is valid only at sufficiently high temperatures. At low temperatures a quantum treatment is necessary and the independence of C_V on T breaks down, as we have already seen.

We next consider an ideal gas consisting of diatomic molecules. Its pressure equation of state is still given by $PV = NkT$ because the pressure depends only on the translational motion of the center of mass of each molecule. However, its heat capacity differs from that of an ideal monatomic gas because a diatomic molecule has additional energy associated with its vibrational and rotational motion. Hence, we expect that C_V for an ideal diatomic gas to be greater than C_V for an ideal monatomic gas.

10.4.2 The Maxwell Velocity Distibution

So far we have used the tools of statistical mechanics to calculate macroscopic quantities of interest in thermodynamics such as the pressure, the temperature, and the heat capacity. We now apply statistical mechanics arguments to gain more detailed information about classical systems of particles by calculating the velocity distribution of the particles.

Consider a classical system of particles in equilibrium with a heat bath at temperature T. We know that the total energy can be written as the sum of two parts: the kinetic energy $K(\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$ and the potential energy $U_{pot}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$. The kinetic energy is a quadratic function of the momenta $\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N$ (or velocities), and the potential energy is a function of the positions $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$ of the particles. The total energy is $E = K + U_{pot}$. The probability density of a microstate of N particles defined by $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N$ is given in the canonical ensemble by

$$P(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = A \exp\left[-\frac{K(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)}{kT}\right] \exp\left[-\frac{U_{pot}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{kT}\right]$$

where A is a normalization constant. The probability density P is a produce of two factors, one that depends only on the particle positions and the other that depends only on the particle momenta. This factorization implies that the probabilities of the momenta and positions are independent. The probability of the positions of the particles can be written as

$$f(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N = B \exp\left[-\frac{U_{pot}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{kT}\right] d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N$$

and the probability of the momenta is given by

$$f(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N = B \exp\left[-\frac{K(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)}{kT}\right] d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N$$

For notational simplicity, we have denote the two probability densities by f, even though their meaning is different in the above equations. The constant B and C can be found by requiring that each probability be normalized.

We stress that the probability distribution for the momenta does not depend on the nature of the interaction between the particles and is the same for all classical systems at the same temperature. This statement might seem surprising because it might seem that the velocity distribution should depend on the density of the system. An external potential also does not affect the velocity distribution. These statements do not hold for quantum systems, because in this case the position and momentum operators do not commute. Because the total kinetic energy is a sum of the kinetic energy of each of the particles, the probability density $f(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$ is a product of terms that each depend on the momenta of only one particle. This factorization implies that the momentum probabilities of the various particles are independent. These considerations imply that we can write the probability that a particle has momentum $\vec{p}$ in the range $d\vec{p}$ as

$$f(p_x, p_y, p_z) dp_x dp_y dp_z = c \exp\left[-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mkT}\right] dp_x dp_y dp_z$$

The constant c is given by the normalization condition

$$c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left[-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mkT}\right] dp_x dp_y dp_z = c \left(\int_{-\infty}^{\infty} \exp\left[-\frac{p^2}{2mkT}\right] dp\right) = 1$$

Completing the integration, we find that $c = (2\pi m k T)^{-3/2}$. Hence the momentum probability distribution can be expressed as

$$f(p_x, p_y, p_z)dp_x dp_y dp_z = \frac{1}{(2\pi m k T)^{3/2}} \exp\left[-\frac{(p_x^2 + p_y^2 + p_z^2)}{2mkT}\right] dp_x dp_y dp_z$$

The corresponding velocity probability distribution is given by

$$f(v_x, v_y, v_z)dv_x dv_y dv_z = \left(\frac{m}{2\pi k T}\right)^{3/2} \exp\left[-\frac{(v_x^2 + v_y^2 + v_z^2)}{2kT}\right] dv_x dv_y dv_z$$

The above expression is known as the **Maxwell velocity distribution**. Note that the form of the probability distribution is a Gaussian. Because $f(v_x, v_y, v_z)$ is a product of three independent factors, the probability of the velocity of a particle in a particular direction is ***independent of the velocity in any other direction***. For example, the probability that a particle has a velocity in the x-direction in the range v_x to $v_x + dv_x$ is

$$f(v_x)dv_x = \left(\frac{m}{2\pi k T}\right)^{1/2} \exp\left[-\frac{v_x^2}{2kT}\right] dv_x$$

Many textbooks derive the Maxwell velocity distribution for an ideal classical gas and give the misleading impression that the distribution applies only if the particles are noninteracting. We stress that the Maxwell velocity (and momentum) distribution applies to any classical system regardless of the interactions, if any, between the particles.

To determine the distribution of speeds for a three-dimensional system, we need to know the number of microstates between v and $v + \Delta v$. This number is proportional to the volume of a spherical shell of width Δv or $4\pi(v + \Delta v)^3/3 - 4\pi v^3 \to 4\pi v^2 \Delta v$ in the limit $\Delta v \to 0$. Hence, the probability that a particle has a speed between v and $v + dv$ is given by

$$f(v)dv = 4\pi A v^2 e^{-mv^2/2kT} \, dv$$

where A is a normalization constant. Using the normalization condition

$$\int_0^\infty f(v)dv = 1$$

to calculate A, it can be shown that

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right) e^{-mv^2/2kT} \, dv$$

This is known as the **Maxwell speed distribution.** Using the Maxwell speed distribution, it can be shown that the mean speed in a classical system of particles is

$$\langle v \rangle = \frac{1}{N} \int_0^\infty v \, f(v)dv = \sqrt{\frac{8kT}{\pi m}}$$

Likewise, the mean square velocity is

$$\langle v^2 \rangle = \frac{1}{N} \int_0^\infty v^2 \, f(v)dv = \frac{3kT}{m} \Rightarrow v_{rms} = \sqrt{\frac{3kT}{m}}$$

where v_{rms} is the root mean square speed. The most probable velocity $\tilde{v}$ is obtained by maximizing $f(v)$,

$$\frac{df(v)}{dv} = 0 \Rightarrow \tilde{v} = \sqrt{\frac{2kT}{m}}$$
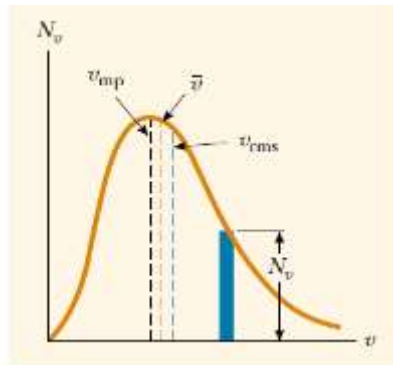

Figure 10.3 The Maxwell speed distribution of gas molecules at some temperature

Suppose we wanted to determine the number of gas molecules with a speed in the range from 400 to 410 m/s. The Maxwell-Boltzmann distribution function states that the speed distribution (1) depends on mass and temperature; (2) peaks in the vicinity of v_{rms}; and (3) few molecules are expected to have speeds much less than or much greater than v_{rms}, as shown in Figure 10.3. Consider the speed distribution curves for N_2 at $T = 300 \, K$ and $T = 900 \, K$, shown

in Figure 10.4. Note that the peak in the curve shifts to the right as T increases, indicating that the average speed increases with increasing temperature.
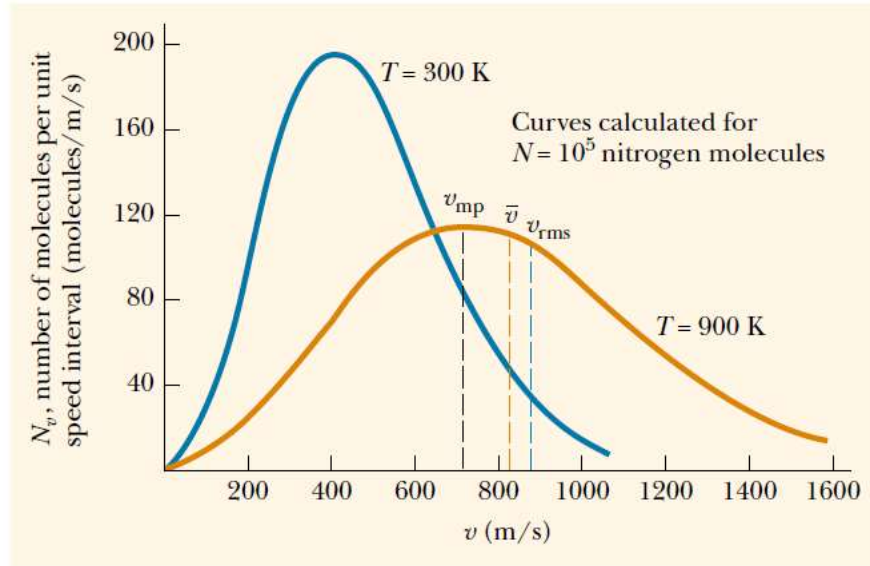

Figure 10.5 The Maxwell speed distribution for 10^5 nitrogen molecules at 300 K and 900 K

10.5 The van der Waals Gas in the Semiclassical Limit

If we relax the assumption that make a gas "ideal", i.e., if we take into account the non-zero molecular size as well as the electromagnetic interaction between molecule we get the "real" gas, the energy of the system of molecules can always be written as

$$E = \sum_i \frac{p_i{}^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} u_{ij}(r_{ij})$$

where i labels the molecules and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the separation vector between the molecules. The intermolecular interaction u_{ij} is repulsive at very short distances (on the order of the molecular size) and is attractive at large distances (i.e. when the molecular separation is greater than the molecular size). Using the classical form of the partition function, we have

$$Z_N = \frac{1}{h^{3N} N!} \int d^3\vec{r}_1 \dots d^3\vec{r}_N d^3\vec{p}_1 \dots d^3\vec{p}_N \times \exp\left[-\beta\left(\sum_i \frac{p_i{}^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} u_{ij}(r_{ij})\right)\right]$$

Performing the momentum integrals, we are left with

$$Z_N = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}\int d^3\vec{r}_1 \dots d^3\vec{r}_N \times \exp\left[-\frac{\beta}{2}\sum_{i<j}u_{ij}(r_{ij})\right] \equiv \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}Z_U$$

As one can easily see, the difficulty is in evaluated the spatial integrals. Let us therefore concentrate on evaluating Z_U.

$$Z_U = \int d^3\vec{r}_1 \dots d^3\vec{r}_N \times \exp\left[-\frac{\beta}{2}\sum_{i<j}u_{ij}(r_{ij})\right]$$

Since $\langle U_{pot}\rangle = -\partial \ln Z_U / \partial\beta$ where $U_{pot} = \sum_{i<j}u_{ij}(r_{ij})$, we can write

$$\ln Z_U = -\int_0^\beta \langle U(\beta')\rangle\, d\beta' + const.$$

At high temperatures ($\beta \to 0$), note that $Z_U = V^N$, which is the same result as the monatomic ideal gas. Therefore, the integration constant is given by $N\ln V$ and thus, we have

$$\ln Z_U = -\int_0^\beta \langle U_{pot}(\beta')\rangle\, d\beta' + N\ln V$$

Now there are $N(N-1)/2$ terms in the sum defining U_{pot} and it is reasonable to assume that each term contributes, say $\langle u_{pot}\rangle$ to the sum in the mean. Therefore, we have

$$\langle U_{pot}\rangle \approx \frac{1}{2}N(N-1)\langle u_{pot}\rangle \approx \frac{N^2}{2}\langle u_{pot}\rangle$$

This is called the **mean field approximation**. We can now write

$$\ln Z_U \approx N\ln V - \frac{N^2}{2}\int_0^\beta \langle u_{pot}\rangle\, d\beta$$

and calculate the mean pair interaction potential from

$$\langle u_{pot} \rangle \equiv \frac{\int_V d^3\vec{r}\, u(r) e^{-\beta u(r)}}{\int_V d^3\vec{r}\, e^{-\beta u(r)}} = -\frac{\partial}{\partial\beta} \ln\left[\int_V d^3\vec{r}\; e^{-\beta u(r)}\right]$$

$$= -\frac{\partial}{\partial\beta} \ln\left[\int_V d^3\vec{r}\left[1 + \left(e^{-\beta u(r)} - 1\right)\right]\right] \equiv -\frac{\partial}{\partial\beta} \ln[V + I(\beta)]$$

Therefore, we have

$$\langle u_{pot} \rangle = -\frac{\partial}{\partial\beta} \ln\left[1 + \frac{I(\beta)}{V}\right] = -\frac{\partial}{\partial\beta}\left[\frac{I(\beta)}{V} + O\left(\frac{I(\beta)}{V}\right)^2\right]$$

If we now integrate with respect to β to get Z_U, we find that

$$\ln Z_U \approx N \ln V - \frac{N^2}{2}\int_0^\beta \langle u_{pot} \rangle \, d\beta = N \ln V + \frac{N^2}{2}\int_0^\beta \frac{\partial}{\partial\beta}\left[\frac{I(\beta)}{V} + O\left(\frac{I(\beta)}{V}\right)^2\right] d\beta$$

$$= N \ln V + \frac{N^2}{2}\left[\frac{I(\beta)}{V} + O\left(\frac{I(\beta)}{V}\right)^2\right]$$

The partition function under the mean field approximation becomes

$$\ln Z = \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) - \ln N! + \ln Z_U \approx \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln\frac{V}{N} + N + \frac{N^2}{2}\left[\frac{I(\beta)}{V} + O\left(\frac{I(\beta)}{V}\right)^2\right]$$

Using the partition function under the mean field approximation, we obtain the average internal energy and pressure

$$\langle U \rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{3N}{2\beta} - \frac{N^2}{2}\frac{\partial}{\partial\beta}\ln\left[\frac{I(\beta)}{V} + O\left(\frac{I(\beta)}{V}\right)^2\right]$$

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{N}{\beta V} - \frac{N^2}{2\beta}\frac{I(\beta)}{V^2} + O\left[\left(\frac{N}{V}\right)^3\right]$$

which are all in terms of the integral $I(\beta)$, which we must now attempt to evaluate.

Notice that the corrections to the ideal gas equation of state are in the form of a Taylor expansion in the number density $n = N/V$

$$P = \frac{n}{\beta}\left(1 + B_2(T)n + B_3(T)n^2 + \cdots\right)$$

This is why this approximation is valid at low densities. The temperature dependent coefficients are called **virial coefficients** and it is our task to evaluate them in this mean field approximation. This expansion is called the **virial expansion**.

If we ignore all particle interactions (i.e. a 1st order approximation of the virial expansion), then $P = n/\beta = nkT$, which is the equation of state for the ideal gas. We will now demonstrate that the van der Waals model is a 2nd order approximation of the virial expansion. To do this, we must determine $I(\beta)$. We will calculate $I(\beta)$ using an approximation of the Lennard-Jones potential, given by

$$u(r) = \begin{cases} \infty & r < r_0 \\ u_0 \left(\dfrac{r_0}{r}\right)^s & r > r_0 \end{cases}$$

When $r < r_0$, the potential is infinite and $e^{-\beta u} = 0$ so we have

$$I(\beta) \equiv 4\pi \int_0^{r_0} r^2 \left[e^{-\beta u(r)} - 1\right] dr \approx -\frac{4\pi}{3} r_0{}^3$$

On the other hand, when $r > r_0$, the temperature is high (β is small) and so is the pairwise potential. Thus, we have

$$I(\beta) \equiv 4\pi \int_0^{r_0} r^2 \left[e^{-\beta u(r)} - 1\right] dr \approx 4\pi \int_0^{r_0} r^2 [1 - \beta u(r) - 1] = 4\pi\beta u_0 r_0^s \int_0^{r_0} r^{2-s} \, dr$$
$$\approx \frac{4\pi\beta u_0 r_0{}^3}{s-3}$$

where we have assumed that $s > 3$ so that the integral is convergent. This gives us an approximation for the second virial coefficient

$$B_2(T) = -\frac{1}{2} I(\beta) = \frac{2}{3}\pi r_0{}^3 \left[1 - \frac{3\beta u_0}{s-3}\right] = b'[kT - a']$$

Here $b' = 2\pi r_0^3/3$ characterizes the molecular volume and $a' = 3\beta u_0/(s-3)$ characterizes the interaction strength. To this approximation, we have

$$P \approx \frac{n}{\beta} + B_2(T)n^2 = nkT + b'[kT - a']n^2$$

Rearranging terms gives

$$P + a'b'n^2 = nkT(1 + nb') \approx \frac{nkT}{1 - nb'} = \frac{kT}{\frac{1}{n} - b'}$$

assuming that $nb' \ll 1$. Therefore, we have

$$(P + a'b'n^2)\left(\frac{1}{n} - b\right) = kT$$

and rewriting the number density as the inverse volume per particle, we have

$$\left(P + \frac{a'b'}{v^2}\right)(v - b') = kT$$

This is the **van der Waals equation of state**. The constant b' is very obviously the "size" of the molecules. The constant $a'b'$ depends on a' which is connected both to the strength, u_0, and the concavity (via s) of the potential when $r > r_0$. It therefore characterizes the strength and range of the intermolecular forces.

Ch. 11 Introduction to Quantum Statistics

We apply the general formalism of statistical mechanics developed previously to weakly interacting quantum systems, leading to quantum statistics. In this chapter, we will provide a broad introduction to the major topics in quantum statistical mechanics. In particular, we will discuss the single particle density of states, the Fermi-Dirac and Bose-Einstein distribution functions, blackbody radiation, and the thermodynamics of degenerate Fermi gases. We will start with a discussion on the grand canonical ensemble.

11.1 The Grand Canonical Ensemble

In the canonical ensemble, if we relax the condition that no matter is exchanged between the system and its reservoir, we obtain the **grand canonical ensemble**. In this ensemble, therefore, the systems are all in thermal equilibrium with a heat reservoir at some fixed temperature, T, but they are also able to exchange particles with this reservoir. Such systems are said to be **open**. Assume that the system, A, is in thermal equilibrium with a reservoir, R and that together they form an isolated system with total energy E_{total} and total number of particles N_{total}. Both E_{total} and N_{total} are fixed. Assume also that A is tiny compared to R. Then we might ask: what is the probability of finding A in a given state, r, with energy E_r and containing N_r particles? If A has energy E and N particles, then the total number of states available to the combined system is

$$\Omega(E, N) = \Omega_A(E, N)\Omega_R(E_{total} - E, N_{total} - N)$$

In the ensemble we are considering, each system is in contact with a heat reservoir at a fixed temperature, T, and each is able to exchange particles with the reservoir. Since the combined system belongs to a microcanonical ensemble, the probability of finding our system with energy E and N particles is given by

$$P(E, N) = \frac{\Omega_A(E, N)\Omega_R(E_{total} - E, N_{total} - N)}{\sum_{E_i, N_i} \Omega_A(E_i, N_i)\Omega_R(E_{total} - E_i, N_{total} - N_i)}$$
$$= C\Omega_A(E, N)\Omega_R(E_{total} - E, N_{total} - N)$$

Since the reservoir is very large compared with our system, then $E \ll E_{total}$ and $N \ll N_{total}$. Expanding $\Omega_R(E_{total} - E, N_{total} - N)$ in a Taylor series about E_{total} gives

$$\ln P(E, N) = \ln C + \ln \Omega_A(E, N) + \ln \Omega_R(E_{total}, N_{total}) - E \left. \frac{\partial \ln \Omega_R(E', N')}{\partial E'} \right|_{E'=E_{total}, N'=N_{total}}$$

$$- N \left. \frac{\partial \ln \Omega_R(E', N')}{\partial N'} \right|_{E'=E_{total}, N'=N_{total}} + \cdots$$

where we have put $N' = N_{total} - N$ and $E' = E_{total} - E$.

For the combined system, which is in in the microcanonical ensemble, recall that

$$\beta = \left(\frac{\partial \ln \Omega_R}{\partial E'} \right)_{E_{total}, N_{total}}$$

is the temperature of the reservoir and we shall call

$$\mu = -\frac{1}{\beta} \left(\frac{\partial \ln \Omega_R(E', N')}{\partial N'} \right)_{E_{total}, N_{total}}$$

the chemical potential of the reservoir. Writing $\ln P(E, N)$ in terms of β and μ gives the required probability

$$\ln P(E, N) = \ln C + \ln \Omega_A(E, N) + \ln \Omega_R(E_{total}, N_{total}) - \beta E + \beta \mu N + \cdots$$

$$\Rightarrow P(E, N) \approx C \Omega_R(E_{total}, N_{total}) \Omega_A(E, N) \exp[-\beta(E - \mu N)]$$

$\Omega(E, N)$ is the number of states available to A at a fixed E and N – the degeneracy. Since the combined system is in the microcanonical ensemble, then the probability of finding A in any one state r of energy $E = E_r$ and particles $N = N_r$ is given by

$$P_r(E_r, N_r) = const. \times \exp[-\beta(E_r - \mu N_r)]$$

Each of the exponential factors is called a **Gibbs factor**. If we define the constant as $1/\mathcal{Z}$, then for any state r, the probability is given by

$$P_r(U_r, N_r) = \frac{1}{\mathcal{Z}} \exp[-\beta(U_r - \mu N_r)]$$

This is the **Gibbs distribution** and it characterizes the grand canonical ensemble. Systems belonging to the grand canonical ensemble have variable contents. This occurs often in many physically interesting situations. For instance, consider the diffusion of molecules across a semi-permeable membrane that separates two containers, A and B. We can adjust the

intermolecular separation of the partition is such that only molecules of one type may pass through. If we wish to speak of A and B individually as thermodynamic systems, we must take into account the fact that their contents vary as one of the gases diffuses across the membrane. Another situation in which we may wish to treat systems with varying contents as thermodynamic systems is when we consider phase transformations. Consider the melting of ice or the boiling of water. In either of these processes, the substance (ice or water) is changing phase from solid to liquid or liquid to gas. If we want to treat the ice and water (or water and water vapor) as separate thermodynamic systems we must account for the fact that the amount of matter contained in each system is continuously changing.

11.2 The Grand Partition Function

The quantity $\mathcal{Z}$ is called the **grand partition function**. By requiring that the sum of the probabilities of all states to equal 1, it can be shown that the grand partition function is given by

$$\mathcal{Z} = \sum_r \exp[-\beta(E_r - \mu N_r)]$$

Similar to the partition function in the canonical ensemble, it can be shown that all the thermodynamic functions can be expressed in terms of the grand partition function and its derivatives.

First, let's determine the internal energy within the grand canonical ensemble.

$$\langle U \rangle = \sum_r P_r U_r = \frac{\sum_r U_r e^{-\beta(U_r - \mu N_r)}}{\sum_r e^{-\beta(U_r - \mu N_r)}} = \frac{1}{\mathcal{Z}} \sum_r U_r e^{-\beta(U_r - \mu N_r)} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

The average number of particles in a given system is given by

$$\langle N \rangle = \sum_r N_r P_r = \frac{\sum_r N_r e^{-\beta(U_r - \mu N_r)}}{\sum_r e^{-\beta(U_r - \mu N_r)}} = \frac{1}{\mathcal{Z}} \sum_r N_r e^{-\beta(U_r - \mu N_r)} = \frac{1}{\beta} \frac{1}{\mathcal{Z}} \frac{\partial}{\partial \mu} \left(\sum_r e^{-\beta(U_r - \mu N_r)} \right)$$

$$= \frac{1}{\beta} \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

The generalized forces are

$$\langle F_\alpha \rangle = \sum_r F_\alpha P_r = -\frac{\sum_r \left(\frac{\partial U_r}{\partial X_\alpha}\right) e^{-\beta(U_r - \mu N_r)}}{\sum_r e^{-\beta(U_r - \mu N_r)}} = -\frac{1}{Z}\sum_r \left(\frac{\partial U_r}{\partial X_\alpha}\right) e^{-\beta(U_r - \mu N_r)}$$

$$= \frac{1}{\beta Z}\frac{\partial}{\partial X_\alpha}\left(\sum_r e^{-\beta(U_r - \mu N_r)}\right) = \frac{1}{\beta Z}\frac{\partial Z}{\partial X_\alpha} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial X_\alpha}$$

From these, we also derive an expression for the entropy as follows. Consider an isothermal quasi-static process in which the partition function undergoes a change dZ. Notice that $Z = Z(\beta, X_\alpha, \mu)$ and one has

$$d\ln Z = \frac{\partial \ln Z}{\partial \beta}d\beta + \sum_\alpha \frac{\partial \ln Z}{\partial X_\alpha}dX_\alpha + \frac{\partial \ln Z}{\partial \mu}d\mu = -\langle U\rangle d\beta + \beta \sum_\alpha \langle F_\alpha\rangle dX_\alpha + \beta\langle N\rangle d\mu$$

Rearranging the above expression (noting that β is held constant in the last term) gives

$$d\ln Z = -d(\beta\langle U\rangle) + \beta d\langle U\rangle - \beta \sum_\alpha \delta W_\alpha + d(\beta\langle N\rangle\mu) - \beta\mu d\langle N\rangle$$

$$\Rightarrow \beta^{-1}d(\ln Z + \beta\langle U\rangle - \mu\beta\langle N\rangle) = d\langle U\rangle - \sum_\alpha \delta W_\alpha - \mu d\langle N\rangle$$

which, comparing the above expression with Gibbs equation for variable contents, means that the left hand side must be associated with the entropy. Therefore,

$$T\,dS = \beta^{-1}d(\ln Z + \beta\langle U\rangle - \mu\langle N\rangle) \Rightarrow S = k(\ln Z + \beta\langle U\rangle - \mu\beta\langle N\rangle)$$

How does this definition of entropy compare to the Boltzmann-Gibbs entropy that we saw last chapter? To see that it reduces the definition, we saw last chapter, we notice that in the canonical ensemble the normalized probability has the form

$$P_r = \frac{e^{e^{-\beta(U_r - \mu N_r)}}}{\sum_s e^{-\beta(U_s - \mu N_s)}} = \frac{1}{Z}e^{-\beta U_r} \Rightarrow \ln P_r = -\beta U_r + \mu\beta N_r - \ln Z$$

which, when substituted into the expression for the Boltzmann-Gibbs entropy, gives

$$S_{Gibbs} = -k\sum_r \frac{e^{-\beta(U_r - \mu N_r)}}{Z}[\beta U_r - \mu\beta N_r + \ln Z] = k(\ln Z + \beta\langle U\rangle - \mu\beta\langle N\rangle)$$

as we expected. We see that indeed the Gibbs definition is more general, under appropriate conditions giving the expressions in the microcanonical ensemble, in the canonical ensemble, and in the grand canonical ensemble.

The other thermodynamic functions also have expressions in terms of $\mathcal{Z}$ and its derivatives. Recall that in the canonical ensemble, the most useful thermodynamic potential was the Helmholtz free energy. Using an analogous argument, it can be shown that the most useful thermodynamic potential is known as the **grand potential:**

$$\Phi_F = F - \sum_s \mu_s N_s = -\frac{1}{\beta} \ln \mathcal{Z}$$

Similar to the Helmholtz free energy, the grand potential is the maximum amount of energy available to do external work for a system in contact with both a heat and a particle reservoir. In other words, the grand potential measures the maximum amount of compression/expansion work and chemical work that a thermodynamic system can produce. Moreover, for a system connected to a heat and particle reservoir, the minimization of the grand potential determines the equilibrium state of the system. We are now in a position to compare the statistical ensembles used to study statistical mechanics

Ensemble	Macrostate	Probability Distribution	Fundamental Surface
Microcanonical	U, V, N	$P_S = 1/\Omega$	$S(U, V, N) = k \ln \Omega$
Canonical	T, V, N	$P_S = e^{-\beta E_s}/Z$	$F(T, V, N) = -kT \ln Z$
Grand Canonical	T, V, μ	$P_S = e^{-\beta(E_s - \mu N_s)}/\mathcal{Z}$	$\Phi_F(T, V, \mu) = -kT \ln \mathcal{Z}$

11.3 Bosons and Fermions

Before we study the thermodynamics of quantum systems, it's useful to highlight some relevant points concerning quantum theory.

11.3.1 Wave-Particle Duality

The historical roots of quantum mechanics are intimately entwined with the development of statistical mechanics around the turn of the 20th century. Especially important in this history was the breakdown of the equipartition theorem, both for electromagnetic radiation (the "ultraviolet catastrophe" which will be described later) and for the vibrational energy of solid crystals (evidence by anomalously low heat capacities at low temperature which will be described later as well). However, there is plenty of more evidence for the wave-particle duality of matter and energy on the atomic scale.

If you shine light on a metal surface, it can knock some electrons out of the metal and send them flying off the surface. This phenomenon is called the **photoelectric effect**. To study the photoelectric effect quantitatively, you can put the piece of metal (called a photocathode) into a vacuum tube with another piece of metal (the anode) to catch the ejected electrons. You can then measure either the voltage that builds up as electrons collect on the anode, or the current produced as these electrons run around the circuit back to the cathode as shown in Figure 11.1. This experiment showed that the final voltage, (and hence the maximum electron kinetic energy), is independent of the brightness of the light source. Brighter light ejects *more* electrons, but does not give an individual electron any more energy than faint line. On the other hand, the final voltage *does* depend on the *color* of the light, that is, on the wavelength of the light. In fact, there is a linear relation between the maximum kinetic energy of the ejected electrons and the frequency of the light: $K_{max} = hf - \phi$, where h is Planck's constant and ϕ is a constant that depends on the metal.
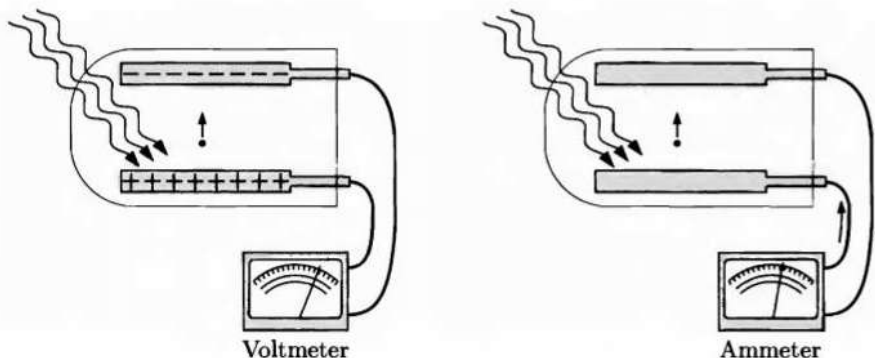

Figure 11.1 Two experiments to study the photoelectric effect. When an ideal voltmeter is connected to the circuit, electrons accumulate on the anode and repel other electrons; the voltmeter measures the energy (per unit charge) that an electron needs to cross. When an ammeter is connected, it measures the number of electrons (per unit time) that collect on the anode and the circulate back to cathode.

Einstein's interpretation of the photoelectric effect was simple: light comes in tiny particles, now called **photons**, each with energy equal to $E_{photons} = hf$. A brighter beam of light contains more photons, but the energy of each photon still depends only on the frequency, not on the brightness. When light hits the photocathode, each electron absorbs the energy of just one photon. The constant ϕ (called the **work function**) is the minimum energy required to get an electron out of the metal; once the electron is free, the maximum energy it can have is the photon's energy minus ϕ.

If light, which was previously thought to be a wave, can behave like a stream of particles, then perhaps it's not surprising that electrons, which were previously thought to be particles, can behave like waves. In other words, if light can have a particle nature, then perhaps electrons can have a wave nature, i.e. electrons undergo diffraction and interference effects. This can be observed through electron diffraction experiments. If we aim a beam of electrons at a pair of

very closely spaced slits, it can be shown that on the viewing screen, electrons will produce an interference pattern, exactly as with light.

The wavelength of the electron beam can be determined from the slit spacing and the size of the interference pattern, just as for light. It turns out that the wavelength is inversely proportional to the *momentum* of the electrons, and the constant of proportionality is Planck's constant: $\lambda = h/p$. This famous relation was predicted in 1923 by Louis de Broglie. It holds for photons too, and there it is a direct consequence of the Einstein relation $E = hf$ and the relation $p = E/c$ between the energy and momentum of anything that travels at the speed of light. De Broglie guessed correctly that electrons (and all other "particles") have wavelengths that are related to their momenta in the same way.
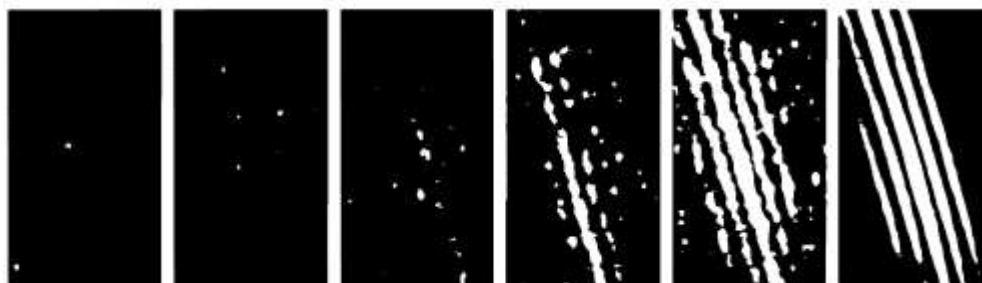

Figure 11.2 These images were produced using the beam of an electron microscope. A positively charged wire was placed in the path of the beam, causing the electrons to bend around either side and interfere as if they had passed through a double slit. The current in the electron beam increases from one image to the next, showing that the interference pattern is built up from the statistically distributed light flashes of individual electrons.

The fact that both electrons and photons can act like waves and produce interference patterns raises some important question. Each individual particle (electron or photon) can land in only one spot on the viewing screen, so if you send the particles through the diffraction apparatus slowly enough, the pattern builds up gradually, dot by dot, as shown in Figure 11.2. Apparently, the place where each particle lands is random with the probability varying across the screen as determined by the brightness of the final pattern. This means that *each* photon or electron must somehow pass through *both* slits and then interfere with *itself* to determine the probability distribution for where it will finally land. In other words, the particle behaves like a wave when passing through the slits, and the amplitude of this wave at the location of the screen determines the probabilities that govern the final position. More precisely, the probability of landing in a particular place is proportional to the square of the final wave amplitude, just as the brightness of an electromagnetic wave is proportional to the square of the electric field amplitude.

11.3.2 Wavefunctions

Given that individual particles can behave like waves, we need a way of describing particles that allows for both particle-like and wave-like properties. For this purpose, physicists have invented the quantum-mechanical **wavefunction** $\Psi(x, y, z, t)$. In describing the "state" of a particle, the wavefunction serves the same purpose in quantum mechanics that the position and momentum vectors serve in classical mechanics: It tells us everything there is to know about what the particle is doing at some particular instant.

A particle can have all sorts of wavefunctions. There are narrow, spiky wavefunctions (corresponding to states in which the particle's position is well defined) and there are also broad, oscillatory wavefunctions (corresponding to states in which the particle's momentum is well defined). In this latter case, the momentum p of the particle is related to the wavelength λ by the de Broglie relation. Actually, the wavelength of the wavefunction tells us only the *magnitude* of the particle's momentum. In order for Ψ to *completely* determine the state of the particle, we need to make it a two-component object, that is, a pair of functions. For a particle with well-defined momentum, the second component has the same wavelength as the first component but it is out of phase by $90^{\mathbf{o}}$ (see Figure 11.3). For Figure 11.3, the momentum is in the x-direction. To give the particle the opposite momentum, we just flip the second component upside down so that it is $90^{\mathbf{o}}$ out of phase in the other direction. The two components of Ψ are normally represented by a single complex-valued function, whose "real part" is the first component and whose "imaginary part" is the second component.
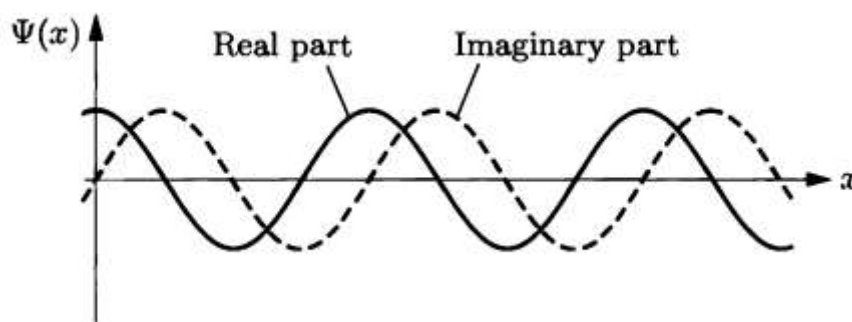

Figure 11.3 A more complete illustration of the wavefunction of a particle with well-defined momentum, showing both the "real" and "imaginary" parts of the function

For any wavefunction, there is a precise interpretation that's very important. First, take your wavefunction and compute its square modulus: $|\Psi(x)|^2 = (Re\ \Psi)^2 + (Im\ \Psi)^2$. *This* function, when integrated between any two points x_1 and x_2, gives you the probability of finding the particle somewhere between those two points if you were to measure its position at that time. Qualitatively, you are more likely to find the particle where its wavefunction is large in magnitude, and less likely to find the particle where its wavefunction is small in magnitude. For

a narrow spiky wavefunction, you're certain to find the particle at the location of the spike, while for a definite-momentum wavefunction you could find the particle absolutely anywhere.

11.3.3 The Uncertainty Principle

Another important type of wavefunction is called a **wavepacket**. A wavepacke is approximately sinusoidal within a certain region but then dies out beyond so it's still reasonably localized in space, as shown in Figure 11.4. For such a wavefunction, both x and p_x are defined approximately, but neither is defined precisely. If we were to measure the position of a particle in such a state, we could get a range of values. If we had a million particles, all in this same state, and we measured their positions, the values would center around some average with a spread that we could quantify by taking the standard deviation Δx of all the values obtained. Similarly, if we had a million particles all in the same state and we measured their momenta, the values would center around some average with a spread that we could quantify by taking the standard deviation Δp_x.
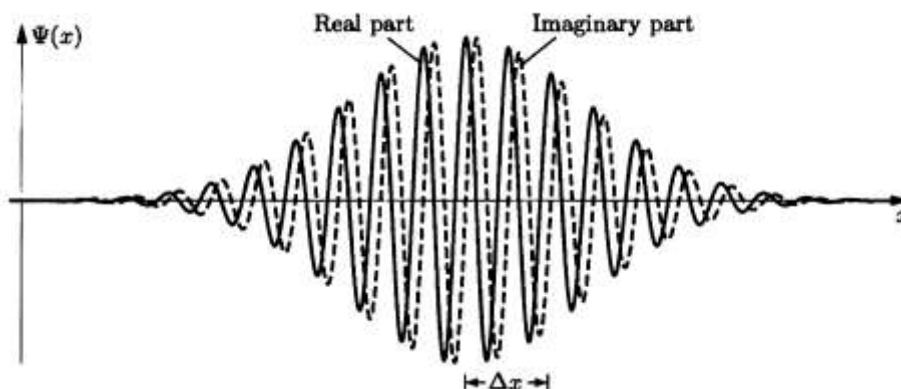

Figure 11.4 A wavepacket, for which x and p_x, are defined approximately but not precisely. The "width" of the wavepacket is quantified by Δx

We could easily construct a wavepacket with a smaller Δx, just by making the oscillations die out more rapidly on each side. However, there is a price: We then get fewer complete oscillations, so the wavelength and momentum of the particle become more poorly defined. By the same token, to construct a wavepacket with a precisely defined momentum we have to include many oscillations, resulting in a large Δx. There's an inverse relation between the width of the wavepacket in position space and its width in momentum space. To be more precise about this relation, suppose we make a wavepacket so narrow that it includes only one full oscillation before dying out. Then the spread in position is roughly one wavelength, while the spread in momentum is quite large, comparable to the momentum itself:

$$\Delta p_x \sim p_x = \frac{h}{\lambda} \sim \frac{h}{\Delta x}$$

Because a smaller Δp_x implies a larger Δx, the relation $\Delta x \Delta p_x \sim h$ actually applies to any wavepacket, not just a very a narrow one.

More generally it can be shown that for any wavefunction whatsoever

$$\Delta x \Delta p_x \geq \frac{h}{4\pi}$$

This is the famous **Heisenberg uncertainty principle**. It says that if you prepare a million particles with identical wavefunctions, then measure the positions of half of the particles and the momenta of the other half and compute the standard deviations, the produce of the standard deviations can't be less than $h/4\pi$. Therefore, no matter how you prepare a particle, you can't put it into a state in which *both* Δx and Δp_x arbitrarily small.

11.3.4 Definite-Energy Wavefunctions

As you can tell from the preceding illustrations, the number of possible wavefunctions that a particle can have is enormous. This poses a problem in statistical mechanics, where we need to *count* how many states are available to a particle. There is no sensible way to count all the wavefunctions; what we need is a way to count *independent* wavefunctions. If a wavefunction Ψ can be written in terms of two others Ψ_1 and Ψ_2, such as

$$\Psi(x) = a\Psi_1(x) + b\Psi_2(x)$$

for some (complex) constants a and b, then we say that Ψ is a **linear combination** of Ψ_1 and Ψ_2. On the other hand, if there are no constants a and b for which the above expression is true, then we say that Ψ is **linearly independent** of Ψ_1 and Ψ_2. What we want to do in statistical mechanics is count the number of linearly independent wavefunctions available to a particle. If the particle is confined within a finite region and its energy is limited, this number is always finite. Even so, there are many different sets of linearly independent wavefunctions that we can work with. Usually, though, it is more convenient to use wavefunctions with definite energy $E = p^2/2m + V(x)$.

To find the definite-energy wavefunctions for a given potential energy $V(x)$, you have to solve a differential equation called the **time-independent Schrodinger equation**. This equation

and methods of solving it are discussed at length in quantum mechanics textbooks. Here, we will look at the solution for a very important special case.

The simplest nontrivial potential energy function is the "infinite square well"

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & else \end{cases}$$

This idealized potential confines the particle to the region between 0 and L, a one dimensional box. Within the box there is no potential energy, while outside the box the particle cannot exist since it would have to have infinite energy. This potential energy function is so simple that we can find the definite-energy just by observing boundary conditions. Every allowed wavefunction must be zero outside the box and the definite energy wavefunctions need to go continuously to zero at $x = 0$ and at $x = L$. A few of the definite-energy wavefunctions are shown in Figure 11.5 In order for the wavefunctions to go to zero at *both* ends of the box, only certain wavelengths are permitted. For each of these wavelengths, we can use the de Broglie relation to find the magnitude of the momentum, then compute the energy as $p^2/2m$. Thus, the allowed energies are

$$E_n = \frac{p_n^2}{2m} = \frac{1}{2m}\left(\frac{h}{\lambda_n}\right)^2 = \frac{h^2}{2m}\left(\frac{n}{2L}\right)^2 = \frac{h^2 n^2}{8mL^2}$$

where n is any positive integer. Notice that the energies are quantized: Only certain discretely spaced energies are possible because the number of half wavelengths that fit within the box must be an integer. More generally, any time a particle is confined within a limited region, its wavefunction must go to zero outside this region and have some whole number of "bumps" inside, so its energy will be quantized.
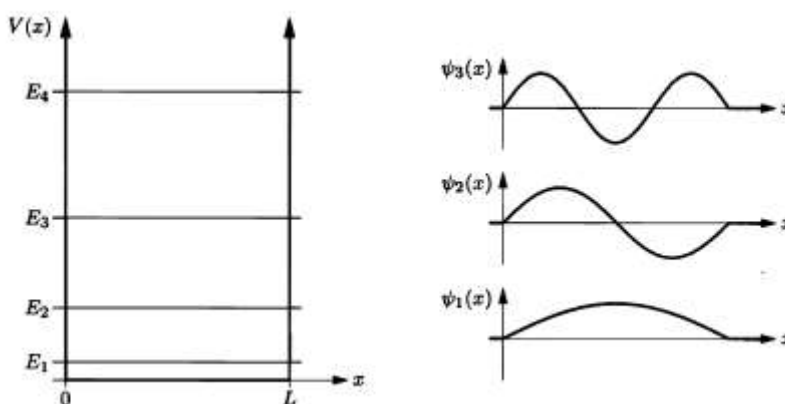

Figure 11.5 A few of the lowest energy levels and corresponding definite-energy wavefunctions for a particle in a one-dimensional box.

Definite-energy wavefunctions are important not just because they have definite energy, but also because any other wavefunction can be written as a linear combination of definite-

energy wavefunctions. Furthermore, the definite-energy wavefunctions are all linearly independent of each other (at least for a particle in one dimension that is confined to a limited region). So counting the definite-energy wavefunctions gives us a convenient way to count "all" the states available to a particle.

For a particle confined inside a three-dimensional box, we can construct a definite-energy wavefunction by taking the product of three 1D definite-energy wavefunctions:

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

These products aren't all the definite-energy wavefunctions, but the others can be written as linear combinations of these, so counting wavefunctions that decompose in this way suffices for our purposes. The total energy also decomposes nicely into a sum of three terms:

$$E = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) = \frac{1}{2m}\left[\left(\frac{hn_x}{2L_x}\right)^2 + \left(\frac{hn_y}{2L_y}\right)^2 + \left(\frac{hn_z}{2L_z}\right)^2\right]$$

where L_x, L_y, and L_z are the dimensions of the box and n_x, n_y, and n_z are any three positive integers. Each triplet of n's yields a distinct linearly independent wavefunction, but not every triplet yields a distinct energy: Most of the energy levels are **degenerate**, corresponding to multiple linearly independent states that must be counted separately in statistical mechanics. The number of linearly independent states that have a given energy is called the **degeneracy** of the level.

11.3.5 Systems of Many Particles

A system of *two* quantum-mechanical particle has only *one* wavefunction. In one spatial dimension, the wavefunction of a two-particle system is a function of two variables, x_1 and x_2, corresponding to the positions of the two particles. More precisely, if you integrate the square of the wavefunction over some range of x_1 *and* over some rang of x_2 values, you get the probability of finding the first particle within the first range and the second particle within the second range. Some two-particle wavefunctions can be factored into a product of single-particle wavefunctions:

$$\Psi(x_1, x_2) = \Psi_a(x_1)\Psi_b(x_2)$$

This is an enormous simplification, which is valid only for a tiny fraction of all two-particle wavefunctions. Fortunately, though it can be shown that all *other* two-particle wavefunctions can

be written as linear combinations of wavefunctions that factor in this way. So if we're only interested in counting linearly independent wavefunctions, we're free to consider only those wavefunctions that factor. (Note: the preceding statement is true whether or not the two particles interact with each other, but if they do *not* interact, there is a further simplification: The total energy of the system is then the sum of the energies of two particles, and if we take Ψ_a and Ψ_b to be the appropriate single-particle definite-energy wavefunctions, then their product will be a definite-energy wavefunction for the combined system.)

If the two particles in question are distinguishable from each other, there's not much more to say. However, quantum mechanics also allows for particles to be absolutely indistinguishable, so that no possible measurement can reveal which is which. In this case, $|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2$. This necessarily implies that $\Psi(x_1, x_2) = \pm\Psi(x_2, x_1)$. This condition actually refers to the states of two different types of particles. For some types of particles, called **bosons**, Ψ is unchanged under interchange of its arguments. For other particles, called **fermions**, Ψ changes sign under this operation. In other words

$$\Psi(x_1, x_2) = \begin{cases} +\Psi(x_2, x_1) & bosons \\ -\Psi(x_2, x_1) & fermions \end{cases}$$

For bosons (fermions), we say that Ψ is symmetric (antisymmetric). Examples of bosons include photons, pions, helium-4 atoms, and many other types of atoms and atomic nuclei. Examples of fermions include electrons, protons, neutrons, neutrinos, and many other types of atoms and nuclei.

The most straightforward application of this property is to the case where both particles are in the same single-particle state, which means $\Psi(x_1, x_2) = \Psi_a(x_1)\Psi_a(x_2)$. For bosons, this equation guarantees that Ψ will be symmetric under interchange of x_1 and x_2. For fermions, this equation guarantees that $\Psi = 0$. Thus, this states two identical fermions cannot occupy the same state, which is known as the **Pauli exclusion principle**.

In many situations, however, it doesn't matter whether the particles in a fluid are bosons or fermions. When the number of available single-particle states is much greater than the number of particles $Z_1 \gg N$, the change of any two particles wanting to occupy the same state is negligible. More precisely, only a tiny fraction of all system states have a significant number of states doubly occupied. For an ideal gas, the single-particle partition function is $Z_1 = VZ_{int}/v_Q$, where Z_1 is some reasonably small number and v_Q is known as the **quantum volume** given by

$$v_Q = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$

Note that the quantum volume is roughly the cube of the average de Broglie wavelength.

Recall in our previous discussion on the ideal gas law in the semiclassical limit that the partition function for a system of N indistinguishable, noninteracting particles was

$$Z = \frac{1}{N!} Z_1^N$$

When two or more particles have a reasonable probability of wanting to occupy the same single-particle state, then this approximation breaks down. The problem is that the counting factor of $N!$, the number of ways of interchanging the particles among their various states, is correct only if the particle are always in *different* single-particle states. The condition $Z_1 \gg N$ for which $Z = Z_1^N / N!$ applies is $/N \gg v_Q$, which states that the ***average distance between particles must be much greater than the average de Broglie wavelength***. For the air we breathe, the average distance between molecules is about 3 nm while the average de Broglie wavelength is less than 0.02 nm, so this condition is definitely satisfied.

What happens when $Z_1 \gg N$ begins to breakdown? Figure 11.6 gives a pictorial representation. Picture each particle as being smeared out in a quantum wavefunction filling a volume equal to v_Q (this is equivalent to putting the particles into wavefunctions that are as localized in space as possible. To squeeze them into narrower wavefunctions, we would have to introduce uncertainties in momentum that are large are large compared to the average momentum h/l_Q, thus increasing the energy and temperature of the system.) In a normal gas, the effective volume thus occupied by all the particles will be much less than the volume of the container. However, if the gas is sufficiently dense or v_Q is sufficiently large, then the wavefunctions will start trying to touch and overlap. At this point it starts to matter whether the particles are fermions or bosons; either way, the behavior will be much different from that of a normal gas.

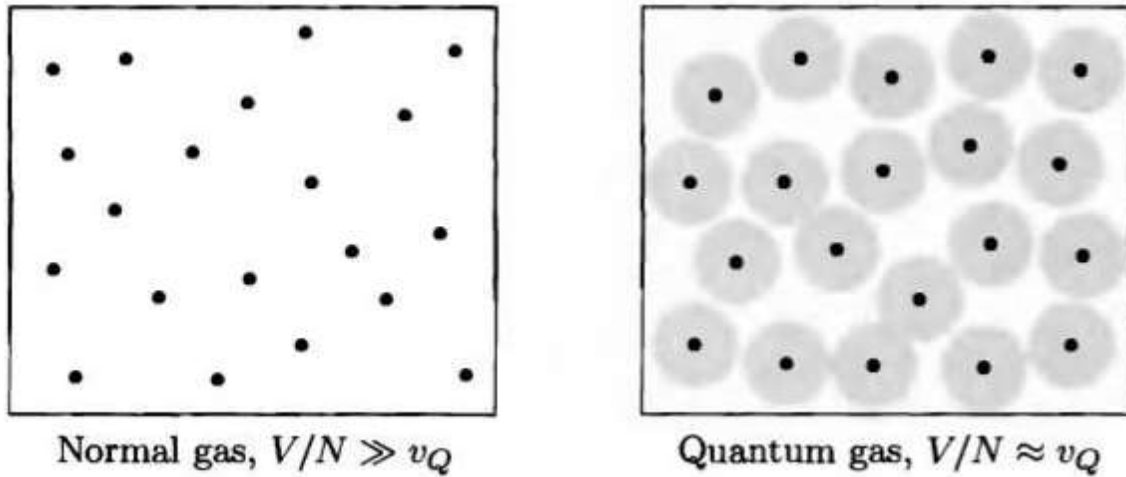Normal gas, $V/N \gg v_Q$ · Quantum gas, $V/N \approx v_Q$

Figure 11.6 In a normal gas, the space between particles is much greater than the typical size of a particle's wavefunction. When the wavefunctions begin to "touch" and overlap, we call it a **quantum gas**.

There are plenty of systems that violate $Z_1 \gg N$, either because they are very dense (such as a neutron start or a white dwarf), or very cold (like liquid helium), or composed of very light particles (such as electrons in a metal or photons in a hot oven). These systems are all within the regime of **quantum statistics** (the study of systems in which 2+ identical particles have a reasonable chance of being in the same single-particle state). The rest of this chapter is devoted to an overview of these systems.

11.4 The Distribution Functions

We now develop the formalism for calculating the thermodynamic properties for systems in which which quantum effects are important. We will begin by considering a system consisting of *one single-particle state*, rather than a particle itself. Thus, the system will consist of a particular spatial wavefunction Ψ. Unlike the classical regime in which we normally work with wavefunctions of definite energy, each of these wavefunctions shares its space with all the other wavefunctions. The "system" and the "reservoir" therefore occupy the same physical space. Moreover, because the particles are indistinguishable for quantum systems, we need to specify the **occupation number n_k**, which is the number of particles in the single particle state k with energy ϵ_k. If we know the value of the occupation number for each single particle microstate, we can write the total energy of system in microstate s as

$$U_s = \sum_k n_k \epsilon_k$$

Thus, the set of n_k completely specifies a microstate of the system.

The probability of a particular microstate is given by the Gibbs distribution

$$P_r(E_r, N_r) = \frac{1}{\mathcal{Z}} \exp[-\beta(E_r - \mu N_r)]$$

To analyze this system, the key idea is that it is possible to distinguish the subset of all particles in a *given single particle microstate* from the particles in all other single particle microstates. For this reason we divide the system of interest into subsystems each of which is the set of all particles that are in a given single particle microstate. Because the number of particles in a given microstate varies, we need to use the grand canonical ensemble and assume that each subsystem is coupled to a heat bath and a particle reservoir independently of the other single particle microstates. Applying this to our system means that we can calculate the grand partition function $\mathcal{Z}_k$ for each subsystem. We write the energy of the n_k particles in the single particle microstate k as $n_k \epsilon_k$ and write $\mathcal{Z}_k$ as

$$\mathcal{Z}_k = \sum_{n_k} \exp[-\beta n_k(\epsilon_k - \mu)]$$

where the sum is over the possible values of n_k. For fermions this sum is straightforward because $n_k = 0, 1$. Therefore, we have

$$\mathcal{Z}_k = 1 + e^{-\beta(\epsilon_k - \mu)}$$

From the grand partition function, we can compute the probability of the state being occupied or unoccupied, as a function of ϵ_k, μ, and T. We can also compute the *average* number of particles in the state (known as the **occupancy** of the state) as

$$\langle N \rangle_k = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln[1 + e^{-\beta(\epsilon_k - \mu)}] = \frac{\beta e^{-\beta(\epsilon_k - \mu)}}{\beta[1 + e^{-\beta(\epsilon_k - \mu)}]} = \left[\exp\left[\frac{(\epsilon_k - \mu)}{kT} \right] + 1 \right]^{-1}$$

This distribution is called the **Fermi-Dirac distribution** and I will label it as $\langle n \rangle_{FD}$. Note the Fermi-Dirac distribution goes to zero when $\epsilon_k \gg \mu$ and goes to 1 when $\epsilon_k \ll \mu$. Thus, states with energy much less than μ tend to be unoccupied and states with energy equal to μ tend to be unoccupied. At very low temperature, fermions will distribute themselves in the energy levels below the chemical potential and all the levels above μ are empty. As the temperature rises, energy levels above the chemical potential begin to be occupied
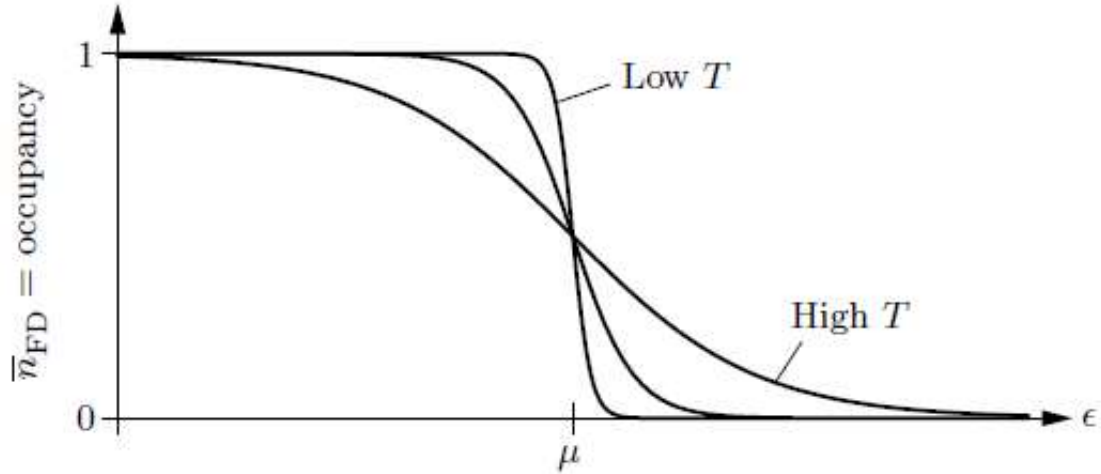
Figure 11.7 The Fermi-Dirac distribution as a function of energy. This plot assumes that $\epsilon_k = \epsilon$

The integer values of n_k are unrestricted for bosons. Thus, the grand partition function is given by

$$\mathcal{Z}_k = \sum_{n_k} \exp[-\beta n_k(\epsilon_k - \mu)] = \sum_{n_k}\{\exp[-\beta(\epsilon_k - \mu)]\}^{n_k}$$

This geometric series converges if $\exp[-\beta(\epsilon_k - \mu)] < 1$. Because this condition must be satisfied for all values of ϵ_k, we require that $e^{\beta u} < 1 \Rightarrow \mu < 0$. In contrast, the chemical potential may be either positive or negative for fermions. The summation of the geometric series gives

$$\mathcal{Z}_k = \sum_{n_k}\{\exp[-\beta(\epsilon_k - \mu)]\}^{n_k} = \frac{1}{1 - \exp[-\beta(\epsilon_k - \mu)]}$$

Therefore, the occupancy in single particle microstate k is given by

$$\langle N \rangle_k = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} = -\frac{1}{\beta}\frac{\partial}{\partial \mu}\ln[1 - e^{-\beta(\epsilon_k - \mu)}] = \left[\exp\left[\frac{(\epsilon_k - \mu)}{kT}\right] - 1\right]^{-1}$$

This distribution is called the **Bose-Einstein distribution** and I will label it as $\langle n \rangle_{BE}$. Like the Fermi-Dirac distribution, the Bose-Einstein distribution goes to zero when $\epsilon \gg \mu$. Unlike the Fermi-Dirac distribution, the Bose-Einstein distribution goes to infinity as $\epsilon \approx \mu$.

The Fermi-Dirac and Bose-Einstein distributions must reduce to the classical limit under the appropriate conditions. In the classical limit $n_k \ll 1$ for all k, which means that the

mean number of particles in any single particle microstate must be small. Hence, $\exp[\beta(\epsilon_k - \mu] \gg 1$ and in this limit the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\langle N \rangle_k = e^{-\beta(\epsilon_k - \mu)}$$

This result is known as the **Maxwell-Boltzmann distribution**. A comparison of all three distributions is given in Figure 11.8. Note that all three distributions agree when $\epsilon - \mu \gg kT$. If we take the lowest-energy state to have $\epsilon \approx 0$, then this condition will be met for all states whenever $\mu \ll -kT$, which is the equivalent to $Z_1 \gg N$.
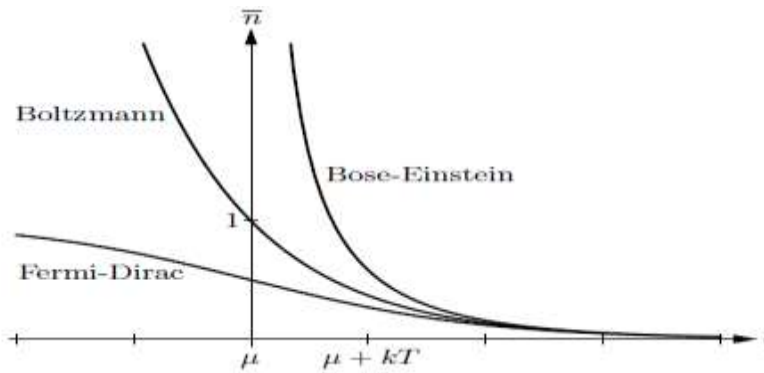

Figure 11.8 Comparison of the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions, all for the same value of μ

We now know how to compute the average number of particles occupying a single-particle state, whether the particles are fermions or bosons, in terms of the energy of the state, the temperature, and the chemical potential. To apply these ideas to any particular system, we still need to know what the energies of all the states are. This is typically a problem that is examined in quantum mechanics, but in these notes, we will deal mostly with particles in a "box", where the wavefunctions are simple sinusoidal functions and the corresponding energies can be determined in a rather straightforward manner.

11.5 Density of States

To find the various thermodynamic quantities we need to calculate various sums. For example, to obtain the mean number of particles in the system over all single particle states:

$$\langle N(T,V,\mu) \rangle = \sum_k \langle N \rangle_k = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1} \qquad (11.1)$$

291

For a given temperature T and volume V, Equation (11.1) is an implicit equation for the chemical potential μ in terms of the mean number of particles. That is, the chemical potential determines the mean number of particles just as the temperature determines the mean energy. Similarly, we can write the mean energy of the system as

$$\langle U(T,V,\mu)\rangle = \sum_k \langle N\rangle_k \epsilon_k$$

For a microscopic system, the number of particles and the energy are well defined, and we will usually replace $\langle N\rangle$ and $\langle U\rangle$ by N and U, respectively. Because we have described the microscopic states at the most fundamental level, that is, by using quantum mechanics, the macroscopic averages of interest involve sums over the microscopic states. However, because the systems of interest are macroscopic, the volume of the system is so large that the energies of the discrete microstates are very close together and for practical purposes indistinguishable from a continuum. As usual, it is easier to do integrals than to do sums over a very large number of microstates, and hence we will replace the sums by integrals. For example, we will write for an arbitrary function $f(\epsilon)$

$$\sum_k f(\epsilon_k) \to \int_0^\infty f(\epsilon)g(\epsilon)d\epsilon$$

where $g(\epsilon)d\epsilon$ is the number of single particle microstates between ϵ and $\epsilon + d\epsilon$. The quantity $g(\epsilon)$ is known as the **density of states**, although a better term would be the density of **single particle microstates**.

Although we have calculated the density of states for a single particle in a box, we review the calculation here to emphasize its generality and the common aspects of the calculation for blackbody radiation. For convenience, we choose the box to be a cube of linear dimension L and assume that there are standing waves that vanish at the faces of the cube. The condition for a standing wave in one dimension is that the wavelength satisfies the condition

$$\lambda = \frac{2L}{n}$$

where n is a nonzero positive integer. It is useful to define the wavenumber k as $k = 2\pi/\lambda$ and write the standing wave condition as $k = n\pi/L$. Because the waves in the x, y, and z directions satisfy similar conditions, we can treat the wave number as a vector whose components satisfy the conditions

$$\vec{k} = \frac{(n_x, n_y, n_z)}{\pi L}$$

where n_x, n_y, and n_z are positive nonzero integers.

Not all values of k are permissible and each combination of (n_x, n_y, n_z) corresponds to a different microstate. In the "number space" defined by the three perpendicular axes labeled by n_x, n_y, and n_z, the possible values of the microstates lie at the centers of cubes of unit edge length. Because the energy of a wave depends only on the magnitude of k, we want to know the number of microstates between k and $k + dk$. Here, it's easier to first find $\Gamma(k)$, the number of microstates with wave number less than or equal to k. We know that the volume in n-space of a single particle microstate is 1, and hence the number of single particle microstates in number space that are contained in the positive octant of a sphere of radius n is given by

$$\Gamma(n) = \frac{1}{8}\left(\frac{4\pi n^3}{3}\right)$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$. Because $\vec{k} = \pi\vec{n}/L$, the number of single particle microstates with wave vector less than or equal to k is

$$\Gamma(k) = \frac{1}{8}\left[\frac{4\pi k^3/3}{(\pi/L)\text{^3}}\right]$$

If we use the relation

$$g(k)dk = \Gamma(k + dk) - \Gamma(k) = \frac{d\Gamma(k)}{dk}dk$$

we obtain

$$g(k)dk = Vk^2\frac{dk}{2\pi^2} \quad (11.2)$$

where the volume $V = L^3$. Equation (11.2) gives the density of states in k-space between k and $k + dk$. Although we obtained the result (11.2) for a cube, the result is independent of the shape of the enclosure and the nature of the boundary condition. That is, if the box is sufficiently large, the surface effects introduced by the box do not affect the physical properties of the system.

The result (11.2) for the density of states in k-space holds for any wave in a three-dimensional enclosure. We next determine the number of states $g(\epsilon)d\epsilon$ as a function of the energy ϵ. For simplicity, we adopt the same symbol to represent the density of states in k-space and in ϵ space because the meaning of g will be clear from the context.

The nature of the dependence of $g(\epsilon)$ on the energy ϵ is determined by the form of the function ϵ_k. For electromagnetic waves of frequency ν we know that $\lambda\nu = c$, $\omega = 2\pi\nu$, and $2\pi/\lambda$. Hence, $\omega = ck$. The energy ϵ of a photon of frequency ω is $\epsilon = \hbar\omega = \hbar ck$. Because $k = \epsilon/\hbar c$, we find from Equation (11.3) that

$$g(\epsilon)d\epsilon = V \, \frac{\epsilon^2}{2\pi^2\hbar^3 c^3} \, d\epsilon$$

The above result requires one modification. The state of an electromagnetic wave or photon depends not only on its wave vector or momentum, but also on its polarization. There are two mutually perpendicular directions of polarization (right circularly polarized and left circularly polarized) for each electromagnetic wave of wavenumber $\vec{k}$. Thus, the number of photon microstates in which the photon has an energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)d\epsilon = V \, \frac{\epsilon^2}{\pi^2\hbar^3 c^3} \, d\epsilon \quad (11.3)$$

11.6 Blackbody Radiation

In classical physics, we treat electromagnetic radiation as a continuous field that permeates all space. Inside a box, we can think of this field as a combination of various standing wave patterns, as shown in Figure 11.9. Each standing-wave pattern behaves as a harmonic oscillator with frequency $f = c/\lambda$. Like a mechanical oscillator, each electromagnetic standing wave has two degrees of freedom with an average thermal energy of kT. Since the total number of oscillators in the electromagnetic field is infinite, the total thermal energy should also be infinite, which is contrary to all experimental results. This disagreement between classical theory and experiment is called the **ultraviolet catastrophe** (because the infinite energy would come mostly from very short wavelengths).

The solution to the ultraviolet catastrophe comes from quantum mechanics. In quantum mechanics, a harmonic oscillator can only have discrete energy levels (measured relative to the ground state energy) $E_n = nhf$, where n is any positive integer. The partition function for a single oscillator is given by

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \cdots = \frac{1}{1 - e^{-\beta hf}}$$

and the average energy is

$$\langle U \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}$$

If we think of the energy as coming in "units" of hf, then the average number of units of energy in the oscillator is

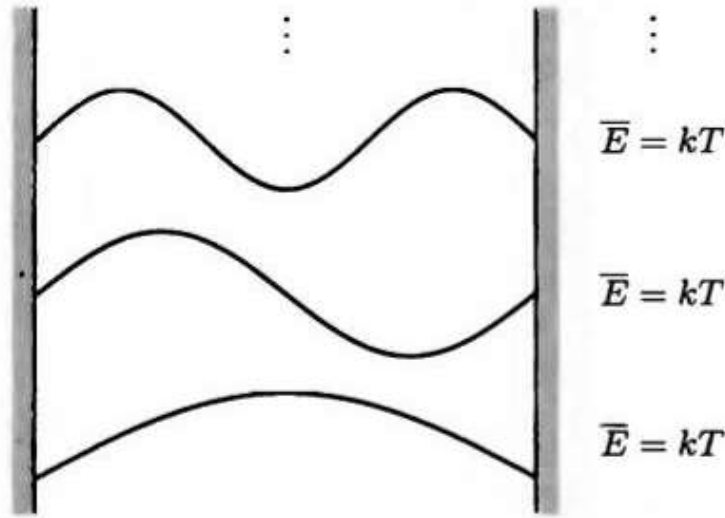$$\langle N \rangle = \frac{1}{e^{hf/kT} - 1}$$

Figure 11.9 Schematic of electromagnetic field in a box as a superposition of standing-wave modes of various wavelengths. Each mode is a harmonic oscillator with some well-defined frequency. Classically, each oscillator should have an average energy of kT. Since the total number of modes is infinite, so is the total energy in the box.

This formula is called the **Planck distribution** (after Max Planck). According to the Planck distribution, short-wavelength modes of the electromagnetic field (with $hf \gg kT$) are *exponentially* suppressed. Thus, the total number of electromagnetic oscillators that effectively contribute to the energy inside the box is finite and the ultraviolet catastrophe does not occur. Notice that this solution *requires* that the oscillator energies be quantized. It is the size of the energy units, compared to kT, that provides the exponential suppression factor.

We can regard electromagnetic radiation as equivalent to a system of non-interacting bosons (photons), each of which has an energy $\hbar\nu$, where ν is the frequency of radiation. If the radiation is in an enclosure, equilibrium will be established and maintained by the interactions of the photons with the atoms of the wall in the enclosure. Because the atoms emit and absorb photons, the total number of photons is not conserved.

If a body in thermal equilibrium emits electromagnetic radiation, this radiation is described as **blackbody radiation** and the object is said to be a **blackbody**. This statement does not mean that the body is actually black. The word "black" indicates that the radiation is perfectly absorbed and re-radiated by the object. The frequency spectrum of light radiated by such an idealized body is described by a universal spectrum called the **Planck spectrum**, which we will derive in this section. The nature of the spectrum depends only on the temperature T of the radiation.

We can derive the Planck radiation law using either the canonical or grand canonical ensemble because the photons are continuously absorbed and emitted by the walls of the container and hence their number is not conserved. This lack of a conservation law for the number of particles implies that the chemical potential vanishes. Since the number of bosons is described by the Bose-Einstein distribution, this implies that the Bose-Einstein distribution reduces to the Planck distribution when $\mu = 0$ for blackbody radiation.

The Planck distribution can be understood by simple considerations. As we have mentioned, equilibrium is established and maintained by the interactions between the photons and the atoms of the wall in the enclosure. The number N of photons in the cavity cannot be imposed externally on the system and is fixed by the temperature T of the walls and the volume V enclosed. Hence, the Helmholtz free energy F for photons cannot depend on N because the latter is not a thermodynamic variable, and we have $\mu = \partial F / \partial N = 0$. If we substitute $\mu = 0$ into the general result for the Bose-Einstein distribution, we find that the mean number of photons in single particle state k is given by the Planck distribution.

Planck's theory of blackbody radiation follows from the form of the density of states for photons found in Equation (11.3). The number of photons with energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$N(\epsilon)d\epsilon = \langle N(\epsilon) \rangle g(\epsilon)d\epsilon = \frac{V}{\pi^2 \hbar^3 c^3} \frac{\epsilon^2 d\epsilon}{e^{\beta \epsilon}-1}$$

If we substitute $\epsilon = h\nu$, we find that the number of photons in the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu)d\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{e^{\beta h\nu} - 1}$$

The distribution of radiated energy is obtained by multiplying the above equation by $h\nu$:

$$E(v)dv = hvN(v)dv = \frac{8\pi hVv^3}{c^3} \frac{dv}{e^{\beta hv} - 1}$$

The above expression gives the energy radiated by a blackbody of volume V in the frequency range between v and $v + dv$. The energy per unit volume $u(v)$ gives the **Planck's radiation law**.

$$u(v) = \frac{8\pi hv^3}{c^3} \frac{1}{e^{hv} - 1} \qquad (11.4)$$

We can change variables to $\epsilon = hv$ and write the energy density as

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}$$

The physical system that most closely gives the spectrum of a black body is the spectrum of the cosmic microwave background, which fits the theoretical spectrum of a blackbody better than the best blackbody spectrum that can be made in a laboratory. In contrast, a piece of hot, glowing firewood is not really in thermal equilibrium, and the spectrum of glowing embers is only a crude approximation to the blackbody spectrum.

The existence of the cosmic microwave background spectrum and its fit to the blackbody spectrum is compelling evidence that the universe experienced a Big Bang. The universe is filled with electromagnetic radiation with a distribution of frequencies given by Planck radiation law with $T \approx 2.725\,K$. This background radiation is a remnant from a time when the universe was composed primarily of electrons and protons at a temperature of about 3000 K. This plasma of electrons and protons interacted strongly with the electromagnetic radiation over a wide range of frequencies, so that the matter and radiation reached thermal equilibrium. As the universe expanded, the plasma cooled until it became energetically favorable for electrons and protons to combine to form hydrogen atoms. Atomic hydrogen interacts with radiation only at the frequencies of the hydrogen spectral lines. As a result most of the radiation energy was effectively decoupled from matter so that its temperature is independent of the temperature of the hydrogen atoms. The background radiation is now at about 2.725 K because of the expansion of the universe. This expansion causes the radiation to be redshifted (i.e. increased the wavelength of the radiation). The temperature of the cosmic radiation background will continue to decrease as the universe expands.

The maximum of $u(v)$ shifts to higher frequencies with increasing temperature. This can be shown by finding the maximum of $u(v)$.

$$\left(\frac{du(\nu)}{d\nu}\right)_{\nu=\nu_{max}} = (3 - \beta h\nu_{max})e^{\beta h\nu_{max}} - 3 = 0$$

This equation can be solved numerically for ν_{max} to give the **Wien's displacement law**

$$\frac{h\nu_{max}}{kT} = 2.822$$

If we make a change of variables from frequency ν to wavelength λ in Planck's radiation law, we can determine the energy emitted by a blackbody at a wavelength between λ and $\lambda + d\lambda$:

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT} - 1} \quad (11.5)$$

In the limit of long wavelengths (or very high temperatures), the term in the exponential becomes small, and the exponential is well approximated with the Taylor series approximation to first order

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda kT} - 1} \approx \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{1 + \frac{hc}{\lambda kT} - 1} = \frac{8\pi hc}{\lambda^4}\frac{d\lambda}{hc}kT = \frac{8\pi kT}{\lambda^4}d\lambda$$

This approximation gives us the **Rayleigh-Jeans law**

$$u(\lambda) = \frac{8\pi kT}{\lambda^4}$$

This result was originally derived from purely classical considerations and it was believed to be the blackbody energy spectrum for all wavelengths. However, note that $u(\lambda) \to \infty$ for small wavelengths. This is the ultraviolet catastrophe, which was discussed previously. Thus, the Rayleigh-Jeans law cannot be cannot be correct for all wavelengths.

In the limit of short wavelengths (or very low temperatures), the exponential term in Equation (11.5) becomes very large and thus, we can approximate (11.5) as

$$u(\lambda)d\lambda \approx \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{\frac{hc}{\lambda kT}}} \Rightarrow u(\lambda) \approx \frac{8\pi hc}{\lambda^5}e^{-\frac{hc}{\lambda kT}}$$

This approximation became known as **Wien's approximation** or **Wien's law**, after Wilhelm Wien who found it by finding a functional form to fit the experimental data.

Integrating Equation (11.4) over all frequencies gives us the total energy emitted by a blackbody

$$u = \int_0^\infty u(\nu)d\nu = \frac{4\sigma}{c}T^4 \Rightarrow E = \frac{4\sigma}{c}VT^4$$

where $u = E/V$ in the above expression. This relation between the total energy and the temperature is known as the **Stefan-Boltzmann law**.

11.6 Degenerate Fermi Gas

As our last introductory topic on quantum statistics, let's consider a "gas" of fermions (i.e. a large collection of free electrons) at very low temperature. In this context, "very low temperature" means that the condition for Boltzmann statistics is violated ($V/N \gg v_Q$) so that $V/N \ll v_Q$. This means that the thermal de Broglie wavelength of the electrons is much larger than the mean interparticle spacing, and hence we must treat the electrons using Fermi statistics. When a system is dominated by quantum mechanical effects, it is said to be \textbf{degenerate}. As we will see, the degenerate Fermi gas model not only gives an excellent model of conduction electrons in a metal, but it also gives us a good description of the thermal properties of the electrons in a white dwarf star and the neutrons in a neutron star.

We first discuss the noninteracting Fermi gas at $T = 0$. At the zero temperature limit ($\beta \to \infty$), the Fermi-Dirac distribution becomes

$$\langle N(\epsilon) \rangle = \begin{cases} 1, & \epsilon < \mu \\ 0, & \epsilon > \mu \end{cases}$$

That is, all states whose energies are below the chemical potential are occupied, and all states whose energies are above the chemical potential are unoccupied. There are numerous consequences to this. At $T = 0$, the system is in its **ground state**, and the particles are distributed among the single particle states so that the total energy of the gas is a minimum. Because we may place no more than one particle in each state, we need to construct the ground state of the system by adding a particle into the lowest available energy state until we have placed all the particles. To find the value of $\mu(T = 0)$, we write

$$N = \int_0^\infty \langle N(\epsilon) \rangle g(\epsilon)d\epsilon \Rightarrow \int_0^{\mu(T=0)} g(\epsilon)d\epsilon = V\int_0^{\mu(T=0)} \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{\epsilon}d\epsilon \quad (11.6)$$

where we have substituted the electron density of states in the above equation. The chemical potential at $T = 0$ is determined by requiring the integral to give the desired number of particles N. Because the value of the chemical potential at $T = 0$ will have special importance, it is common to denote it by ϵ_F:

$$\epsilon_F \equiv \mu(T = 0)$$

where ϵ_F, the energy of the highest occupied state, is called the **Fermi energy**.

The integral on the right hand side of (11.6) gives

$$N = V \int_0^{\mu(T=0)} \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3} \sqrt{\epsilon}\, d\epsilon = \frac{V}{3\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{3/2} \Rightarrow \epsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}$$

where the density $\rho = N/V$. It is convenient to write $\epsilon_F = p_F^2/2m$ where p_F is known as the **Fermi momentum**. It follows that the Fermi momentum p_F is given by

$$p_F = (3\pi^2\rho)^{1/3}\hbar$$

The Fermi momentum can be estimated by using the de Broglie relation $p = h/\bar{\lambda}$ and taking $\bar{\lambda} \sim \rho^{-1/3}$, the mean distance between the particles. That is, the particles are "localized" within a distance of order $\rho^{-1/3}$.

At $T = 0$, all the states with momentum smaller than p_F are occupied and all the states above this momentum are unoccupied. The boundary in momentum space between occupied and unoccupied states at $T = 0$ is called the **Fermi surface**. For an ideal Fermi gas in three dimensions, the Fermi surface is the surface of a sphere with radius p_F. We can understand why the chemical potential at $T = 0$ is positive by reasoning similar to that given for an ideal classical gas. At $T = 0$ the contribution of $T\Delta S$ to the Helmholtz free energy vanishes, and no particle can be added with energy less than $\mu(T = 0)$. Thus, $\mu(T = 0) > 0$. In contrast, we argued that $\mu(T > 0)$ is much less than zero for an ideal classical gas due to the large change in the entropy when adding (or removing a particle). We also find it convenient in the following to introduce a characteristic temperature, the **Fermi temperature** T_F, by $T_F = \epsilon_F/k$.

A direct consequence of the fact that the density of states in three dimensions is proportional to $\epsilon^{1/2}$ is that the mean energy per particle at $T = 0$ is

$$\frac{\langle U \rangle}{N} = \frac{\int_0^{\epsilon_F} \epsilon g(\epsilon)d\epsilon}{\int_0^{\epsilon_F} g(\epsilon)d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2}d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2}d\epsilon} = \frac{\frac{2}{5}\epsilon_F^{5/2}}{\frac{2}{3}\epsilon_F^{3/2}} = \frac{3}{5}\epsilon_F$$

Therefore, the total energy is given by

$$U = \frac{3}{5}N\epsilon_F = \frac{3}{5}N(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\rho^{2/3}$$

The pressure at $T = 0$ can be found from the relation

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial U}{\partial V}\right)_{T,N} = -\frac{3}{5}N^{\frac{5}{3}}(3\pi^2)^{\frac{2}{3}}\frac{\hbar^2}{2m}\frac{\partial}{\partial V}\left(V^{-\frac{2}{3}}\right) = \frac{3}{5}N^{\frac{5}{3}}(3\pi^2)^{\frac{2}{3}}\frac{\hbar^2}{2m}\left(\frac{2}{3}V^{-\frac{5}{3}}\right)$$

$$= \frac{2}{5}\rho\epsilon_F$$

The fact that the pressure is nonzero even at zero temperature is a consequence of the **Pauli exclusion principle**, which allows only one particle to have zero momentum (two electrons if spin is considered). All other particles have finite momentum and hence give rise to a nonzero pressure at $T = 0$. Another way to understand the above relation is to recall the classical pressure equation of state, $P = \rho kT$, which would predict that the pressure is zero at zero temperature. However, if we replace T by the Fermi temperature T_F, then $P \propto \rho kT_F = \rho\epsilon_F$. The degeneracy pressure is what keeps matter from collapsing under the electrostatic forces that attract electrons and protons.

Let's apply the properties of a degenerate Fermi gas to white dwarfs and neutron stars. A star that has consumed all its nuclear fuel will undergo gravitational collapse, but may end up in a stable state as a **white dwarf** or a **neutron star**. This occurs when the mass that remains in the core after the outer layers are blown away does not exceed a particular limit, called the **Chandrashekar limit**. Stars that succeed in forming such stable remnants owe their existence to the high degeneracy pressure exerted by electrons (for white dwarfs) and neutrons (for neutron stars).

A white dwarf star can be considered as a degenerate electron gas. The nuclei present within the white dwarf balance the charge and provide the gravitational attraction that holds the star together. The total kinetic energy of the degenerate electrons is given by the Fermi energy

$$U_{kinetic} = \frac{3}{5}N\epsilon_F = \frac{3}{5}N \cdot \left[\frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3}\right]$$

301

If we assume that the star contains one proton and one neutron for each electron, then $N = M/2m_p$, where m_p is the mass of a proton and M is the total mass of the star, and thus we have

$$U_{kinetic} = \frac{3}{5}N \cdot \left[\frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}\right] = \frac{3}{5}\left(\frac{M}{2m_p}\right) \cdot \left[\frac{h^2}{8m_e}\left(\frac{3M}{2\pi m_p V}\right)^{2/3}\right]$$

Finally, if we assume a spherical white dwarf, then $V = (4/3)\pi R^3$. Therefore, we have

$$U_{kinetic} = \frac{3}{5}\left(\frac{M}{2m_p}\right) \cdot \left[\frac{h^2}{8m_e}\left(\frac{3M}{2\pi m_p V}\right)^{2/3}\right] = \frac{3}{5}\left(\frac{M}{2m_p}\right) \cdot \left[\frac{h^2}{8m_e}\left(\frac{9M}{8\pi^2 m_p R^3}\right)^{2/3}\right]$$

$$= \frac{3h^2}{40m_e}\left(\frac{M}{2m_p}\right)^{5/3}\left(\frac{9}{4\pi^2 R^3}\right)^{2/3} = 0.0088\frac{h^2 M^{5/3}}{m_e m_p^{5/3}R^2}$$

The Fermi energy and Fermi temperature for the white dwarf star is given by

$$\epsilon_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3} = \frac{h^2}{8m_e}\left(\frac{9M}{8\pi^2 m_p}\right)^{2/3}\frac{1}{R^2}$$

$$T_F = \frac{\epsilon_F}{k}$$

Here, R is the equilibrium radius of a white dwarf star, which can be determined by finding the minimum of the total energy . It can be shown that the gravitational potential energy of a white dwarf is given by

$$U_{grav} = -\frac{3}{5}\frac{GM^2}{R}$$

Thus, the total energy of a white dwarf can be given by

$$U_{total} = U_{kinetic} + U_{grav} = -\frac{3}{5}\frac{GM^2}{R} + 0.0088\frac{h^2 M^{5/3}}{m_e m_p^{5/3}R^2}$$

The equilibrium radius of a white dwarf is determined by the minimum of the total energy

$$0 = \frac{d}{dR}\left[-\frac{3}{5}\frac{GM^2}{R} + 0.0088\frac{h^2 M^{5/3}}{m_e m_p^{5/3}R^2}\right] \Rightarrow R = (0.029)\frac{h^2}{Gm_e m_p^{5/3}}\frac{1}{M^{1/3}}$$

For a one solar mass white dwarf $M = 2 \times 10^{30}\ kg$, $R = 7200\ km$ and thus, the Fermi energy and the Fermi temperature for the white dwarf star is given by

$$\epsilon_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{2/3} = \frac{h^2}{8m_e}\left(\frac{9M}{8\pi^2 m_p}\right)^{2/3}\frac{1}{R^2} = 1.9 \times 10^5\ eV$$

$$T_F = \frac{\epsilon_F}{k} = 2.3 \times 10^9\ K$$

For a sense of scale, this is more than a hundred times hotter than the center of the sun. It seems unlikely that the actual temperature of a white dwarf star would be anywhere near this high. In other words, the thermal energy of the electrons is almost certainly much smaller than the kinetic energy they have even at $T = 0$. This indicates that the degenerate Fermi gas model is a good model for the white dwarf star. Thus, the degeneracy pressure for the white dwarf star is

$$P = \frac{2}{5}\rho\epsilon_F = \frac{2}{5}\left(\frac{M}{\frac{4}{3}\pi R^3}\right) \cdot \frac{h^2}{8m_e}\left(\frac{9M}{8\pi^2 m_p}\right)^{\frac{2}{3}}\frac{1}{R^2}$$

This indicates that the electron degeneracy pressure increases as the radius of the white dwarf shrinks as expected. As the star contracts, all the lowest energy levels are filled and the electrons are forced into higher and higher energy levels, filling the lowest unoccupied energy levels. This creates an effective pressure which prevents further gravitational collapse.