Chapter 1

Introduction

1.1 Energy

Despite its fundamental usefulness, energy is a concept that is difficult to define. The most practical, though not very informative or insightful, definition of energy is that it is a scalar quantity associated with the state of an object or collection of objects. The definition of the state (or condition) of an object or collection of objects naturally depends upon the scale of the investigation. For example, when describing the energy of a book lying on a desk we might be interested in the energy associated with the position of the book relative to the surface of the Earth, with the energies associated with the individual atoms that constitute the book, or perhaps all of these energies. As in other physics courses, We will consider two main forms of energy: energy that is associated with the motion of an object, called *kinetic energy* and denoted by the variable K, and energy associated with the position of an object, called *potential energy* and denoted by the variable U. The variable E will typically be used to denote the total energy of a system.

1.2 Microscopic vs Macroscopic

Let's make a distinction between the sizes of the systems and/or the properties of these systems that we describe. We will use the term microscopic to describe a system that consists of only a few objects or a system whose physical size is small (*e.g.*, roughly the dimensions of a single molecule). We will use the term macroscopic to describe a system that consists of a large number of objects (*e.g.*, the number of molecules of air in the room) or a system whose physical size is large (*e.g.*, visible without the use of a microscope). For example, a block sliding across a frictionless horizontal surface would be considered a macroscopic system, whereas the atoms that constitute that block would be a microscopic system. Similarly we can now make a distinction between microscopic and macroscopic descriptions of our system. For example, the magnitude of the movements of the atoms within a block relative to each other would be

a microscopic description of the block, whereas the volume of the block would be a macroscopic description. Thus, macroscopic parameters characterize the system as a whole and provide a statistical description of ensemble behavior of the microscopic objects that constitute the system.

1.3   Statistical Descriptions of Systems

The energy of a macroscopic system of N objects could be calculated as a summation of the kinetic and potential energies of each object in the system. If we use subscript i to denote these objects, we can express the total energy of the system as

$$E = \sum_i E_i \quad \rightarrow \quad E = \sum_i K_i + (K_{rot})_i + U_i$$

In this equation, E_i is the total energy of the ith object in the system, K_i is the kinetic energy of the ith object in the system which is a sum of all possible kinetic energies (translational and rotational), and U_i is the total potential energy of the ith object in the system, which is a sum of all the possible potential energies (gravitational, spring, *etc.*).

Now let's consider a macroscopic system that consists of a 100 ml of water in a sealed container. Rather than a collection of blocks, this system consists of approximately 3×10^{24} molecules of water. Each of these molecules will have kinetic energies and potential energies, and each molecule can interact with other molecules in the system (through collisions, *e.g.*). The energy of this system is simply the sum of the kinetic and potential energies of all these molecules of water, just as it was for the system of N objects discussed above. Sadly, however, the sheer number of terms in this summation makes this approach impractical. Furthermore, even if you had a computer powerful enough to perform all calculations necessary to calculate the energy of this system and the associated differentiation necessary for calculating the kinematics of the molecules of water you would still be unable to apply this approach. Such a complete deterministic description of this system is impossible because of the limitations imposed by quantum mechanics on the ability to precisely determine the position and velocity of an object.

We can, however, derive a valid statistical description of the ensemble system of water molecules that includes a representation of the average behavior of the individual molecules. If we could follow an individual molecule of water in the system for a long enough period of time that molecule would eventually have been located in all possible positions in the container and would eventually have had all possible kinetic energies. Naturally, while we are following one specific molecule of water all of the other molecules of water are also moving around in the container and thus also eventually experiencing all possible positions and kinetic energies. Given the very large number of water molecules in our system we can reasonably argue that at any instant of time all possible positions and kinetic energies are associated with at least one molecule of water. This

argument is fundamental to statistical descriptions of macroscopic systems. It can be more generally expressed as

> If the number of objects in a system is large enough then all possible positions and kinetic energies accessible to the objects in the system will be associated with at least one object in the system.

It follows that a system is equally likely to be found with its microscopic constitute objects in any of the possible configurations that are compatible with the macroscopic parameters of the system. For example, the volume of the container constrains the volume of the water, which, in turn, places limits on the possible positions (*i.e.*, possible configurations) of the water molecules. Let's refer to each configuration of the microscopic objects in the system as a *thermodynamic state* (or simply state) of the system.

> **Thermodynamic state**: a configuration of the microscopic constituent objects in a macroscopic system. Thermodynamic states can be characterized using the associated macroscopic parameters of the entire system.

For example, each distribution of the molecules of water associated with the total volume of water would constitute a state of the system. If the volume of the water remains constant then each of these states are equally probable. In other words, if we could identify and label the individual molecules of water in this system there would be an equal probability of each molecule to be found in any of the possible positions within the solution of water, and moving with any of the possible velocities, such that the total volume of the water was 100 ml. Furthermore, each configuration of the molecules of water that would correspond to a total volume of 100 ml would be called an *accessible state* for the system.

> **Accessible state**: a microstate that is compatible with the macroscopic parameters of the system.

We define a system to be in *thermal equilibrium* if the probability of finding a system with in any of its accessible states is constant in time.

> In **thermal equilibrium** the probability of finding a system in any of its accessible state is independent of time. Furthermore, each of the accessible states of a system is equally probable when the system is in thermal equilibrium.

System Energy

Since systems in equilibrium are equally likely to be found in any of their accessible states we can define the average energy for a system $\overline{E}$ to be equal to the product of the number of objects in the system N and the average energy of each object in the system $\overline{\epsilon}$.

$$\overline{E} = N\overline{\epsilon}$$

Strictly speaking, this equation will be valid only for systems consisting of large numbers of objects, like our system of water molecules. For all of the thermodynamic systems we will consider, this condition can be assumed to be satisfied, although the calculation of $\overline{\epsilon}$ is not always straightforward.

The energy of the system is also a *state function*. This means that the energy depends upon the arrangement of the system (*i.e.*, the positions and movement of the objects in the system) but does not depend upon the process by which the system arrived at its arrangement (*i.e.*, how each object obtained its position and movement).

> **State function**: a property of a system that depends upon only the arrangement of the system.

State functions are also exact differentials.

Equation of State

We define the set of parameters necessary to define the thermodynamic state of a system to be *state variables*.

> **State variables**: the set of parameters required to define a thermodynamic state.

State variables are parameters that can be measured directly in the laboratory (volume, *e.g.*) or that can be inferred from such measurements. Although the appropriate set of state variable varies between systems, each system is defined by a specific set of relationships between its corresponding state variables. We refer to these relationships as the *equations of state* for the system.

> **Equation of state**: an expression of the relationship between the state variables for a system.

In addition to volume, the energy, temperature, and pressure of a system are common state variables found in equations of state.

1.4   Energy Conservation

Energy has a very interesting fundamental property: it can neither be created nor destroyed. This property of energy is referred to as the law of conservation of energy, which is also referred to as the 1ˢᵗ law of thermodynamics. Energy can be converted from one type to another or transferred between objects, however. For example, the potential energy of a skydiver is converted into kinetic energy as she falls toward the ground. Or during a collision the kinetic energy of one car may be transferred to the kinetic energy of another car.

We can divide changes in energy or transfers of energy into those which occur within a system and those that result from interactions between the system and something outside the system (more generally, with the environment outside the system). If all external interactions with the outside environment are prevented, the system is referred to as an ***isolated system***.

> **Isolated system**: a system for which interactions with the outside environment are prevented. The total energy of an isolated system is constant.

The total energy of an isolated system is constant. Any energy conversion that occurs for an isolated system must occur within the system and not involve interactions between the system and the outside environment.

Work, Heat, and the First Law of Thermodynamics

In non-isolated systems energy is exchanged with the outside environment. A change in energy of a system that results from a mechanical is referred to as *work*.

> **Work**: a change in energy associated with a mechanical interaction. Work is denoted by the variable W.

Friction and drag are both examples of mechanical interactions (*i.e.*, pushes or pulls). We refer to the change in energy associated with non-mechanical interactions as heat.

> **Heat**: a change in energy associated with a non-mechanical interaction. Heat is denoted by the variable Q.

A relationship between work, heat, and the changes in the energy of a system is described in Equation 1.1.

$$\Delta E = Q - W \qquad (1.1)$$

In this equation, a positive value for Q denotes heat absorbed by the system from the environment and a negative value for Q denotes heat released by the system to the environment. A positive value for W denotes work done by the system on the environment and a negative value for W denotes work done on the system by the environment. Equation 1.1 is a statement of energy conservation and is typically referred to as the 1st law of thermodynamics.

Equation 1.1 can also be expressed in differential form as

$$dE = đQ - đW \qquad (1.2)$$

The symbol $đ$ denotes that heat and work are inexact differentials. This is in contrast to energy, which is an exact differential.

1.5   Conjugate Variables

We learned in classical mechanics that the differential amount of work done by a force acting over a differential displacement is given by the equation

$$\bar{d}W = \vec{F} \cdot d\vec{r}$$

We can generalize this expression to thermodynamics by considering *generalized forces* and *generalized displacements*. These forces and their associated displacements are called conjugate variables. In thermodynamics, the thermodynamic "force" is always an intensive variable and the "displacement" is always an extensive variable[1]. We will also assume that an intensive variable is the partial derivative of the internal energy with respect to the associated extensive variable, while all other variables are held constant.

We need to be careful here, of course, since in the context of thermodynamics we are concerned by the work done by a system. Thus, the work done by a system associated with its pressure acting over a change in the system's volume is given by the following expression:

$$\bar{d}W = PdV$$

The work is therefore positive if the volume of the system increases and the work is negative if the volume of the system decreases.

The energy of a system can also change if the number of particles in the system changes. We describe the work associated with this process in terms of the *chemical potential* of the system, denoted by μ, and the change in the number of particles in the system, denoted as dN.

$$\bar{d}W = -\mu dN$$

The extra negative sign is here due to historical definitions.

Thus, if the only work possible for a system results from a change in the volume of the system or a change in the number of particles of the system, the 1$^{\text{st}}$ law of thermodynamics in the context of that system can be written as

$$dE = \bar{d}Q - PdV + \mu dN$$

For this equation the conjugate variables are:

- Pressure (P) and Volume (V) $\rightarrow$ $P = -\left(\frac{\partial E}{\partial V}\right)_N$

- Chemical Potential (μ) and Particle Number (N) $\rightarrow$ $\mu = \left(\frac{\partial E}{\partial N}\right)_V$

The subscripts indicate which variables are held constant in the partial derivative. For example, $\left(\frac{\partial E}{\partial V}\right)_N$ is the partial derivative of the energy with respect to volume when the number of particles is held constant.

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[1]Recall that extensive parameters scale with the size of the system, but intensive parameters do not.

The intensive variables in these expressions are pressure and chemical potential. The extensive variables are volume and particle number. Thus, the pressure and chemical potential are the generalized forces, which drive the generalized displacements in volume and particle number, respectively. Another way of interpreting this is that pressure reflects the change in the energy of the system associated with a change in the volume[2] of the system, and chemical potential reflects the change in the energy of the system associated with a change in the number of particles in the system.

Several other conjugate variables that are sometimes used to describe dW for a system are:

- Electric Potential (V_e) and Electric Charge (q)

- Magnetization (M) and Magnetic Field (H)

- Surface Tension (σ) and Area of Stretched Material (A)

- Elastic Force (F) and Length of Stretched Material (L)

We will learn later that dQ can also be written as a conjugate pair.

1.6 Heat Capacity

Heat capacity is a measure of how the temperature of a system changes when that system absorbs or releases heat. A common definition of heat capacity is shown in Equation 1.3.

$$C = \frac{dQ}{dT} \tag{1.3}$$

We can rewrite this expression using Equation 1.2.

$$C = \frac{dE + dW}{dT} \quad \rightarrow \quad C = \frac{dE}{dT} + \frac{dW}{dT}$$

Moving forward with the derivations in this section, let's assume that we are dealing with a system where the only work that can be done is associated with a change in the volume of the system

$$dW = PdV \quad \rightarrow \quad C = \frac{dE}{dT} + P\frac{dV}{dT}$$

This expression is frequently referred to as the heat capacity at constant pressure, denoted as C_P

$$C_P = \frac{dE}{dT} + P\frac{dV}{dT}$$

If the volume of the system is constant, $dV = 0$, and heat absorbed or released by the system will not be associated with any work done by the system. In

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[2]In other words, pressure is probably best thought of as volumetric energy density

this case, we refer to the heat capacity as the heat capacity at constant volume, denoted as C_V.

$$C_V = \frac{dE}{dT}$$

However, it would be better to define these heat capacities using partial derivatives rather than total derivatives. Thus,

$$C_V = \left(\frac{dQ}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad C_P = \left(\frac{dQ}{\partial T}\right)_P \qquad\qquad (1.4)$$

1.7   Summary

- **Thermodynamic state**: a configuration of the microscopic constituent objects in a macroscopic system. Thermodynamic states can be characterized using the associated macroscopic parameters of the entire system.

- **State variables**: the set of parameters required to define a thermodynamic state.

- **Equation of state**: an expression of the relationship between the state variables for a system.

- *Extensive* parameters scale with the size of the system, but *intensive* parameters do not.

- **State function**: a property of a system that depends upon only the arrangement of the system. State functions are also exact differentials

- A thermodynamic *force* is always an intensive variable and a thermodynamic *displacement* is always an extensive variable. The thermodynamic force is the partial derivative of the internal energy of the system with respect to the thermodynamic displacement, while all other variables are held constant.

- The average energy for a system $\overline{E}$ to be equal to the product of the number of objects in the system N and the average energy of each object in the system $\bar{\epsilon}$
$$\overline{E} = N\bar{\epsilon}$$

- **First Law of Thermodynamics**: an expression of energy conservation
$$dE = dQ - dW$$

- Heat capacity is a measure of how the temperature of a system changes when that system absorbs or releases heat
$$C = \frac{dQ}{dT} \qquad C_V = \left(\frac{dQ}{\partial T}\right)_V \qquad C_P = \left(\frac{dQ}{\partial T}\right)_P$$