7. Internal energy and the first law of thermodynamics

7.1 Internal energy: an extensive state variable

A macroscopic system consists of a huge number (roughly on the order of Avogadro’s number, \( N_{\text{Avogadro}} = 6.0 \times 10^{23} \text{ mol}^{-1} \)) of atoms or molecules, and these atoms or molecules are not only moving inside the system but also exerting forces on each other. According to mechanics, classical or quantum, these atoms or molecules then must carry both the kinetic energies due to their motion and the potential energy due to the forces among them. Each macroscopic system therefore stores some energy called “internal energy” \( U \), which is the sum of the total kinetic energy and the total potential energy of all the atoms or molecules in the system that is at rest as a whole. Note that the internal energy does not include the kinetic energy due to the motion of the system as a whole nor the potential energy of the system as a whole due to an external field.

Internal energy is an extensive state variable

Even when a system is exposed to its environment, as long as it is in its equilibrium state so that the temperature \( T \) and the pressure \( P \) of the system are equal to those of the environment (i.e., \( T = T_{\text{environment}} \) and \( P = P_{\text{environment}} \)), its internal energy has a well-defined value on the macroscopic level so that the internal energy is a state variable. Being the sum of the kinetic and the potential energy of the constituent atoms or molecules, the internal energy must be proportional to the total number \( N \) of these atoms or molecules, which is in turn proportional to their mole number: \( U \propto N \propto n \), which implies that the internal energy is extensive so that we can express it as

\[
U = nu(T, P),
\]

where \( u \) is the molar internal energy defined by \( u = U/n \).

Internal energy as a bookkeeping device for energy-exchange processes

There are two main reasons why we are interested in the internal energy of a system. First, the internal energy changes its value when the system exchanges some energy with the outside through heat or work. As mentioned before, understanding processes of energy transfer is one of our major goals in thermal physics as it is important in engineering applications such as designing a heat engine.
Internal energy as a window or a probe to microscopic level

The second reason why we value the internal energy is as follows. By examining the internal energy as a function of the temperature and the pressure of the system, we will learn how the total energy stored inside the system is distributed among different types of kinetic energies (e.g., translational, rotational, and vibrational kinetic energies of diatomic molecules) and potential energies (e.g., the electric potential energy due to attractive forces between conduction electrons and ions, the electric potential energy due to repulsive forces among ions, and the electric potential energy due to repulsive forces among conduction electrons inside a metal) on the microscopic level. The internal energy is thus a window or a probe to the microscopic level and can reveal basic microscopic processes inside the system.

How do we measure the molar internal energy $u(T,P = 1 \text{ atm})$?

To measure the molar internal energy $u(T,P = 1 \text{ atm})$ of a system at the atmospheric pressure, we usually follow the three steps below:

(i) Measure the molar heat capacity at constant pressure $c_p(T,P = 1 \text{ atm})$ (to be defined below).

(ii) Calculate the molar enthalpy $h$, which is a state variable, from $c_p(T,P = 1 \text{ atm})$ by

$$h(T,P = 1 \text{ atm}) = h(T_0,P = 1 \text{ atm}) + \int_{T_0}^{T} c_p(T',P = 1 \text{ atm})dT',$$

where $T_0$ is the temperature of some reference state. This equation shows that from $c_p(T,P = 1 \text{ atm})$, we can calculate only the molar enthalpy difference:

$$\Delta h(T,P = 1 \text{ atm}) = h(T,P = 1 \text{ atm}) - h(T_0,P = 1 \text{ atm}) = \int_{T_0}^{T} c_p(T',P = 1 \text{ atm})dT'.$$

This is not surprising since the enthalpy, as we will see later, is a type of energy and energy in physics gets a well-defined value only after we set its value to be zero at some reference state. For example, when we define the gravitational potential energy of an object near the surface of the earth, we can set it to be zero at the ground level or at the floor level in a room.
In other words, only a difference in the gravitational potential energy when the object is placed at two different locations is physically meaningful.

(iii) Calculate $u(T, P = 1 \text{ atm})$ from $h(T, P = 1 \text{ atm})$ and the equation of state $v = v(T, P = 1 \text{ atm})$ by

$$u(T, P = 1 \text{ atm}) = h(T, P = 1 \text{ atm}) - P v(T, P = 1 \text{ atm}),$$

which in fact follows from the definition of the molar enthalpy:

$$h = u + P v,$$

which we will discuss later. Using the equation for $h(T, P = 1 \text{ atm})$ in terms of $c_p(T, P = 1 \text{ atm})$ given in (ii), we then find

$$u(T, P = 1 \text{ atm}) = u(T_0, P = 1 \text{ atm}) + \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' - P\{v(T, P = 1 \text{ atm}) - v(T_0, P = 1 \text{ atm})\}$$

**Derivation:**

$$u(T, P = 1 \text{ atm}) = h(T, P = 1 \text{ atm}) - P v(T, P = 1 \text{ atm})$$

$$= \left\{ h(T_0, P = 1 \text{ atm}) + \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' \right\} - P v(T, P = 1 \text{ atm})$$

$$= \left\{ u(T_0, P = 1 \text{ atm}) + P v(T_0, P = 1 \text{ atm}) \right\} + \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' - P v(T, P = 1 \text{ atm})$$

$$= u(T_0, P = 1 \text{ atm}) + \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' - P\{v(T, P = 1 \text{ atm}) - v(T_0, P = 1 \text{ atm})\}$$

This equation shows again that using $c_p(T, P = 1 \text{ atm})$ and $v = v(T, P = 1 \text{ atm})$, we can calculate only the molar internal energy difference:
\[
\Delta u(T, P = 1 \text{ atm}) = u(T, P = 1 \text{ atm}) - u(T_0, P = 1 \text{ atm})
= \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' - P\{v(T, P = 1 \text{ atm}) - v(T_0, P = 1 \text{ atm})\}
\]

As discussed in Sec.5.6.4, the equation of state \( v = v(T, P = 1 \text{ atm}) \) is either directly measured (e.g., for gases) or calculated from the coefficient of thermal expansion \( \alpha(T, P = 1 \text{ atm}) \) (e.g., for liquids and solids) so that to estimate \( u(T, P = 1 \text{ atm}) \), we must measure \( c_p(T, P = 1 \text{ atm}) \) and \( v = v(T, P = 1 \text{ atm}) \) or \( \alpha(T, P = 1 \text{ atm}) \).

**All thermal properties from \( c_p(T, P) \) and \( v(T, P) \) (or \( c_p(T, P), \alpha(T, P) \), and \( \kappa(T, P) \))**

As with the internal energy, we can calculate all the thermodynamic quantities of a macroscopic system (including all the state variables mentioned in the last chapter and other quantities such as heat and work during a process) from \( c_p(T, P) \) and \( v(T, P) \) or from \( c_p(T, P), \alpha(T, P) \), and \( \kappa(T, P) \). In other words, \( c_p(T, P), \alpha(T, P) \), and \( \kappa(T, P) \) completely characterize each macroscopic system as far as thermodynamics is concerned.

**SUMMARY FOR SEC.7.1**

1. The internal energy of a macroscopic system is the total energy carried by its constituent molecules or atoms excluding the kinetic energy due to the motion of the system as a whole and the potential energy of the system as a whole due to an external field.

2. The internal energy \( U \) of a system is an extensive state variable so that it can be expressed as \( U = nu(T, P) \), where \( n \) is the mole number of the system and \( u \) is its molar internal energy that depends on its temperature \( T \) and pressure \( P \).

3. The internal energy is important for two main reasons: (1) it is a book-keeping device for energy exchange processes for a system; (2) it allows us to find how the total energy of the system is distributed among different types of kinetic and potential energies on the microscopic level.

4. The molar internal energy of a system under the atmospheric pressure is calculated from its molar heat capacity at constant pressure \( c_p(T, P = 1 \text{ atm}) \) and its equation of state, \( v = v(T, P = 1 \text{ atm}) \):

\[
u(T, P = 1 \text{ atm}) = u(T_0, P = 1 \text{ atm})
+ \int_{T_0}^{T} c_p(T', P = 1 \text{ atm})dT' - P\{v(T, P = 1 \text{ atm}) - v(T_0, P = 1 \text{ atm})\}\]