2.6: The Energy of the System

A large part of classical thermodynamics is concerned with the energy of the system. The total energy of a system is an extensive property whose value at any one instant cannot be measured in any practical way, but whose change is the focus of the first law of thermodynamics (Chap. 3).

2.6.1 Energy and reference frames

Classical thermodynamics ignores microscopic properties such as the behavior of individual atoms and molecules. Nevertheless, a consideration of the classical mechanics of particles will help us to understand the sources of the potential and kinetic energy of a thermodynamic system.

In classical mechanics, the energy of a collection of interacting point particles is the sum of the kinetic energy $\frac{1}{2}mv^2$ of each particle (where m is the particle's mass and v is its velocity), and of various kinds of potential energies. The potential energies are defined in such a way that if the particles are isolated from the rest of the universe, as the particles move and interact with one another the total energy (kinetic plus potential) is constant over time. This principle of the conservation of energy also holds for real atoms and molecules whose electronic, vibrational, and rotational energies, absent in point particles, are additional contributions to the total energy.

The positions and velocities of particles must be measured in a specified system of coordinates called a *reference frame*. This e-book will use reference frames with *Cartesian* axes. Since the kinetic energy of a particle is a function of velocity, the kinetic energy depends on the choice of the reference frame. A particularly important kind is an *inertial* frame, one in which Newton's laws of motion are obeyed (see Sec. G.1 in Appendix G).

A reference frame whose axes are fixed relative to the earth's surface is what this e-book will call a *lab frame*. A lab frame for all practical purposes is inertial (Sec. G.10). It is in this kind of stationary frame that the laws of thermodynamics have been found by experiment to be valid.

The energy E of a thermodynamic system is the sum of the energies of the particles contained in it and the potential energies of interaction between these particles. Just as for an individual particle, the energy of the system depends on the reference frame in which it is measured. The energy of the system may change during a process, but the principle of the conservation of energy ensures that the sum of the energy of the system, the energy of the surroundings, and any energy shared by both, all measured in the same reference frame, remains constant over time.

This e-book uses the symbol E_{sys} for the energy of the system measured in a specified inertial frame. The system could be located in a weightless environment in outer space, and the inertial frame could be one that is either fixed or moving at constant velocity relative to local stars. Usually, however, the system is located in the earth's gravitational field, and the appropriate inertial frame is then an earth-fixed lab frame.

If during a process the system as a whole undergoes motion or rotation relative to the inertial frame, then E_{sys} depends in part on coordinates that are not properties of the system. In such situations E_{sys} is not a state function, and we need the concept of internal energy.

2.6.2 Internal energy

The **internal energy**, U, is the energy of the system measured in a reference frame that allows U to be a state function—that is, at each instant the value of U depends only on the state of the system. This e-book will call a reference frame with this property a *local frame*. A local frame may also be, but is not necessarily, an earth-fixed lab frame.

Here is a simple illustration of the distinction between the energy E_{sys} of a system measured in a lab frame and the internal energy U measured in a local frame. Let the *system* be a fixed amount of water contained in a glass beaker. (The glass material of the beaker is part of the surroundings.) We can define the state of this system by two independent variables: the temperature, T, and pressure, p, of the water. The most convenient local frame in which to measure U in this case is a frame fixed with respect to the beaker.

- Section 3.1.1 will show that the relation between changes of the system energy and the internal energy in this example is $\Delta E_{\text{sys}} = \Delta E_{\text{k}} + \Delta E_{\text{p}} + \Delta U$, where E_{k} and E_{p} are the kinetic and potential energies of the system as a whole measured in the lab frame.

Our choice of the local frame used to define the internal energy U of any particular system during a given process is to some extent arbitrary. Three possible choices are as follows.

- Is it possible to determine a numerical *value* for the internal energy of a system? The total energy of a body of mass m when it is at rest is given by the Einstein relation $E = mc_0^2$, where c_0 is the speed of light in vacuum. In principle, then, we could calculate the internal energy U of a system at rest from its mass, and we could determine ΔU for a process from the change in mass. In practice, however, an absolute value of U calculated from a measured mass has too much uncertainty to be of any practical use. For example, the typical uncertainty of the mass of an object measured with a microbalance, about $0.1\ \mu\mathrm{g}$ (Table 2.2), would introduce the enormous uncertainty in energy of about 10^{10} joules. Only values of the *change* ΔU are useful, and these values cannot be calculated from Δm because the change in mass during an ordinary chemical process is much too small to be detected.

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