The work–energy theorem and the first law of thermodynamics

José María Mínguez
Dpto. de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Aptdo. 644, 48080 Bilbao, Spain
E-mail: wdpmiroj@lg.ehu.es

Abstract This paper presents the first law of thermodynamics, and shows what thermodynamics adds to the work–energy theorem from mechanics. This may help students to understand the contents of the law itself and the significance of both the heat transfer and the internal energy of a system.

Keywords first law; work; heat; internal energy

Introduction

The first law of thermodynamics deals with the energy of a system and how it can vary, whether by means of mechanical work or by a heat flow.

The different forms of energy, as well as the work done by a force, are concepts precisely defined by mechanics. Moreover, there is the work–energy theorem, which states the relationship between the work done on a system and the increase in its kinetic energy. Accordingly, this theorem seems to offer an appropriate basis to define and to understand the new contributions brought in by the first law of thermodynamics.

Nevertheless, in classical texts [1, 2] the work–energy theorem is usually ignored or else used as a starting point to present the thermodynamics first law, but not fully developed. However, as thermodynamics is concerned with processes in which the internal state of a system changes, it is of great interest to consider the work done by the internal forces of the system, as well as the changes in its internal kinetic and potential energies, in order to throw some light on the significance of the so-called internal energy of the system.

The aim of this paper is not to derive the first law of thermodynamics as a byproduct of mechanics, but instead to show what this axiomatic law of thermodynamics adds to the work–energy theorem of mechanics. This can greatly help students understand the first law as set forth in classical texts.

The work–energy theorem

In mechanics, the work–energy theorem demonstrates that the total work done on a system is transformed into kinetic energy. This is represented in a very simple and meaningful equation as follows:

$$W_{\text{total}} = \Delta E_{\text{k}} \quad (1)$$

in which W_{total} is the total work done on the system, including the work carried out by all the external forces (W_{ex}), as well as the work developed by the internal forces within the system (W_{in}). So

$$W_{\text{total}} = W_{\text{ex}} + W_{\text{in}} \tag{2}$$

Now, if the external work is separated into two terms, namely the work done by the external conservative forces ($W_{\text{ex,c}}$), which are associated with an external potential energy ($E_{\text{p,ex}}$), and the non-conservative external work (W'_{ex}), the whole external work can be written as:

$$W_{\text{ex}} = W_{\text{ex,c}} + W'_{\text{ex}} = -\Delta E_{\text{p,ex}} + W'_{\text{ex}} \tag{3}$$

Similarly, the work developed by the internal forces within the system can be also expressed as the sum of a conservative work term plus the non-conservative internal work. So:

$$W_{\text{in}} = W_{\text{in,c}} + W'_{\text{in}} = -\Delta E_{\text{p,in}} + W'_{\text{in}} \tag{4}$$

where $E_{\text{p,in}}$ is the internal potential energy of the system.

As for the kinetic energy of a system, mechanics shows that it can be considered as consisting of two terms, as follows:

$$E_{\text{k}} = \frac{1}{2} M v_{\text{CM}}^2 + E_{\text{k,CM}} \tag{5}$$

M being the total mass of the system, v_{CM} the velocity of its center of mass, and $E_{\text{k,CM}}$ the kinetic energy of the system with respect to its center of mass. The first term on the right-hand side of equation 5 represents the kinetic energy of the center of mass of the system, as if it had the mass of the whole system. Thus, as the velocity v_{CM} is taken with respect to an external reference frame, this first term can be called the external kinetic energy of the system ($E_{\text{k,ex}}$), whereas the second term would be its internal kinetic energy ($E_{\text{k,in}}$). Accordingly, the increase of the kinetic energy of a system can be written in the following way:

$$\Delta E_{\text{k}} = \Delta E_{\text{k,ex}} + \Delta E_{\text{k,in}} \tag{6}$$

Then, the substitution of equations 2, 3, 4 and 6 into equation 1 allows us to order terms as follows:

$$W'_{\text{ex}} = \Delta E_{\text{p,ex}} + \Delta E_{\text{k,ex}} + \Delta E_{\text{p,in}} + \Delta E_{\text{k,in}} - W'_{\text{in}} \tag{7}$$

Equation 7 is a general developed expression of the work–energy theorem derived from mechanics. It should be noticed that, though it does not describe the details of the energetic terms, each of them is explicitly stated, which will be of great help both to define and to understand the contribution of thermodynamics when establishing the first law.

Heat flow

W'_{ex}, on the left-hand side of equation 7, is the external non-conservative work done on the system. This means that it cannot be associated with the variation of any sort of potential energy.

Mechanics precisely defines the work done by a system A over a system B as:

$$W = \int \vec{F} \overrightarrow{ds} \tag{8}$$

where $\vec{F}$ and $\overrightarrow{ds}$ are respectively the force exerted by A on B and the displacement of such a force, whatever the origin of the force may be.

In any case, the quantification of work, as defined by mechanics, requires the identification of both the macroscopic working force and its displacement.

At this point thermodynamics discloses the possibility of work being performed by some non-macroscopic forces. This kind of work would correspond to the definition given by equation 8, but in practice cannot be calculated by such an equation. In fact, though not identifiable as macroscopic work, since no macroscopic force performs it, it is real work and may result in a macroscopic transfer of energy as much as mechanical work.

The energy transferred by microscopic forces between two systems is identified by thermodynamics as heat transfer. So, it could be referred to as micro-thermic work, in contrast to the macroscopic work characterized by equation 8. Instead, such micro-thermic work has been traditionally named as heat flow, Q, whereas the term 'work', or W, has been reserved for macroscopic work.

As a consequence and with respect to mechanics, thermodynamics extends the concept of work to an energy transfer, which may include a heat flow. So, the left-hand side of equation 7 can be written as

$$W'_{ex} = W + Q \tag{9}$$

this being the first contribution of thermodynamics when establishing the first law.

State of a system

In general, the configuration of a system is described by a set of extensive variables, the reversible variation of which involves an exchange of work between the system and its surroundings, but not a change in the external potential and kinetic energies of the system. Typical configuration variables are the volume (V) of a system, the total magnetization (m) of a long rod in an external magnetic field parallel to its length, or the total polarization (P) of a dielectric slab under an electric field, among others. According to equation 8, the elemental work performed on the system in the respective processes, in which these variables are reversibly changed, is given in each case by:

$$\delta W = -p\mathrm{d}V$$

$$\delta W = H\mathrm{d}m$$

$$\delta W = E\mathrm{d}P \tag{10}$$

where p, H and E are intensive variables of the system (i.e. the pressure, the magnetic intensity, and the electric intensity, respectively).

It is understood that, if more than one configuration variable is reversibly changed, the work done on the system may be expressed as:

$$\delta W = \sum Y \mathrm{d} X \tag{11}$$

where X represents the successive configuration extensive variables of the system, and Y stands for the respective intensive variables. Evidently, the work done on a system depends on the process it follows, which is described in each case by the curve $Y = Y(X)$.

Any equilibrium state of a system, with a fixed composition, may be described by the concerned pairs of variables (X, Y) and by the most characteristic variables of thermodynamics, which are the temperature, T, and the entropy, S. However, given the equations of state

$$Y = Y(S, X) \quad \text{and}$$

$$T = T(S, X) \tag{12}$$

only half of these variables are independent, this set of independent variables being sufficient for defining the equilibrium state of the thermodynamics system.

Internal energy

As for the right-hand side of equation 7, the last three terms refer to the internal state of the thermodynamic system.

The sum

$$E_{\mathrm{p,in}} + E_{\mathrm{k,in}} = E_{\mathrm{mech,in}} \tag{13}$$

is the internal mechanical energy of the system, determined, as deduced from mechanics, by the relative positions of its particles, whatever these particles may be, and by their velocities relative to the center of mass. Consequently, the internal mechanical energy of a system depends only on the internal state of the system and so the variation of the internal mechanical energy, in a process from equilibrium state 1 to 2, will depend only on the extreme states of the process and not on the way the system runs between them. This is found by mechanics and may be expressed as:

$$\Delta E_{\mathrm{mech,in}} = \Delta E_{\mathrm{p,in}} + \Delta E_{\mathrm{k,in}} = E_{\mathrm{mech,in,2}} - E_{\mathrm{mech,in,1}} \tag{14}$$

At this point thermodynamics defines a new function of state, U, the variation of which between states 1 and 2 can be written:

$$\Delta U = \Delta E_{\mathrm{p,in}} + \Delta E_{\mathrm{k,in}} - W'_{\mathrm{in}} = \Delta E_{\mathrm{mech,in}} - W'_{\mathrm{in}} = U_2 - U_1 \tag{15}$$

This proposition is the second contribution of thermodynamics on the way to establishing the first law.

The new function, U, which deducts from the variation of the internal mechanical energy of the system the work developed by the internal non-conservative forces, is identified by thermodynamics as the internal energy of the system.

Mechanics establishes that the potential energy of a system, as well as its kinetic energy, are functions of the state of the system. The novelty of the proposition of thermodynamics lies in the fact of defining a new function of the internal state of a system, the variation of which includes non-conservative work.

General form of the first law

Taking the two contributions of thermodynamics, reflected in equations 9 and 15, into the result of the work–energy theorem, as derived from mechanics in equation 7, the following equation can be written:

$$W + Q = \Delta E_{\text{p,ex}} + \Delta E_{\text{k,ex}} + \Delta U \qquad (16)$$

which is the general form of the first law of thermodynamics. Equation 16 states that the energy transfer between the system and its surroundings, both by macroscopic work as well as by heat flow, equals the increase in the external potential and kinetic energy of the system plus the increase in its internal energy.

Now, as the external mechanical energy depends only on the external state of the system, whereas the internal energy depends on the internal state, the total energy of the system:

$$E = E_{\text{p,ex}} + E_{\text{k,ex}} + U \qquad (17)$$

is a function of the state of the system, whose variation in a process

$$\Delta E = \Delta E_{\text{p,ex}} + \Delta E_{\text{k,ex}} + \Delta U = E_2 - E_1 \qquad (18)$$

depends only on the initial and final states the process goes between. Accordingly, the general form of the first law of thermodynamics (equation 16) can be rewritten as follows:

$$\Delta E = W + Q \qquad (19)$$

As a consequence, although the macroscopic work done on the system while it passes from one state to another depends on how the process is performed and cannot be computed as any change of a function of state, and neither can the heat flow, the sum of $W + Q$ is equal to the variation of the total energy of the system, which is a function of state.

The first law of thermodynamics

Thermodynamics is largely concerned with processes in which there is no change in either the external kinetic energy or the external potential energy of a system. In this case the variation of the energy of the system, as given by equation 18, can be simply expressed as:

$$\Delta E = \Delta U = U_2 - U_1 \tag{20}$$

and equation 19 is reduced to:

$$\Delta U = W + Q \tag{21}$$

which is commonly referred to as the analytical form of the first law of thermodynamics.

From what has been said, it is evident that the work carried out on a system and the heat flow exchanged are not functions of its state, but depend on the process the system follows. Moreover, such work and heat are not any properties of the system, but have the only meaning of being different forms of energy transfer between the system and the surroundings in a process.

Therefore, the elemental values of the work and of the heat flow are not exact differentials. Hence, the typical way of writing the differential version of equation 21 is:

$$\mathrm{d}U = \delta Q + \delta W \tag{22}$$

Concluding remarks

The work–energy theorem of mechanics offers a very appropriate basis for establishing and understanding the first law of thermodynamics. Thermodynamics generalizes the work–energy theorem by including the heat flow into a system within the work performed on it, as a transfer of energy.

Furthermore, approaching the first law of thermodynamics from mechanics allows us to identify in a very simple way the constituent terms of the internal energy of a system. There are three such terms, namely, the internal potential energy, the internal kinetic energy and the internal non-conservative work the system develops in a process.

From mechanics theory it would be deduced that the change in both the internal kinetic energy and the internal potential energy of a system in a process depends only on the extreme equilibrium states of the process. The work–energy theorem also identifies the internal work, but does not prove that it depends only on the extreme states of the process. It is the role of thermodynamics to show from experience that the variation of the three terms as a whole depends only on the extreme states of the process, from which the internal energy of a system is defined and the first law is established.

References

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