

Introducing thermodynamics through energy and entropy

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We suggest a simple approach to introducing thermodynamics, beginning with the concept of internal energy of deformable bodies. From a series of thought experiments involving ideal gases, we show that the internal energy depends on the volume and on a second parameter, leading to the development of the concept of entropy. By introducing entropy before the notions of temperature and heat, the proposed approach avoids some of the major conceptual difficulties with the traditional presentation. The relationship between mechanics and thermodynamics naturally emerges, mechanics corresponding to isentropic thermodynamics. The questions of evolution to equilibrium and irreversibility are studied under the light of the action of the “dynamic force” and its dissipative character, evincing the benefits of keeping in mind the microscopic picture. © 2012

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I. INTRODUCTION

Thermodynamics is one of the key disciplines of physics and chemistry, yet in its traditional form it continues to elicit intellectual resistance. Despite being well established for many years and dealing with apparently simple and intuitive concepts, thermodynamics remains quite difficult and subtle.

We believe the difficulties with thermodynamics arise essentially from two main factors. The first one is the traditional development using the variable *temperature*. As is well known, the natural variables associated with the internal energy U are the *volume* and the *entropy*. We can then Legendre-transform U into the other thermodynamic potentials that flank it on the “thermodynamic square,”¹ and obtain temperature from these potentials via Maxwell’s relations. A formulation of thermodynamics that starts with $U = U(S, V)$ contributes to a neat mathematical derivation and an easier understanding of the meaning of the different symbols. An early introduction of the entropy was also proposed by Callen.²

A second difficulty comes from the fact that thermodynamic quantities such as temperature and pressure are defined in equilibrium. The application of the formalism to non-equilibrium processes makes several variables and notions lose their intuitive physical meaning and the mere use of the words denoting these variables may induce errors. The difference between the static and dynamic pressures is crucial and is thoroughly discussed in this paper.

Herein, we suggest a way to avoid most of the traps frequently encountered in the presentation of thermodynamics. To this purpose, we try to maintain a natural and strong connection with mechanics and the microscopic view. We start by making the link between mechanical energy and the internal energy of deformable bodies in Sec. II. In Sec. III, we use a simple “base model” involving an ideal gas to show that the internal energy cannot be a function only of the deformation variable. However, unlike the conventional presentation of thermodynamics in which the variable temperature is a cornerstone, here it is entropy that is immediately introduced as the additional required variable. The relationship with mechanics is then direct: mechanics is isentropic thermodynamics. The second law and the questions of evolution to equilibrium and irreversibility are also addressed in Sec. III. Heat and the first law of thermodynamics are introduced in

Sec. IV, from generalizations to the base model. That section also discusses the adiabatic piston as an example to illustrate the advantages of the proposed approach and discusses some further extensions of the model. The main findings are reviewed and discussed in Sec. V.

II. WORK AND ENERGY: MECHANICS AND THERMODYNAMICS

The concepts of *work* and *energy* were developed empirically, associated first with the notions of *force*, *gravitational potential energy*, and *kinetic energy*. The complexity of the action of muscles was replaced with a simplified description of a static force, which can be measured, for instance, by a dynamometer. This led to an understanding of *weight* as a force, and of the corresponding opposing force present in equilibrium. The concepts of work of the weight and work of the force opposing weight appear naturally from here. The idea of gravitational potential energy arises from the design and construction of weight-lifting machines.

These intuitive concepts are a fundamental part of any introductory study of physics. Among many excellent textbooks, we would like to recall the brilliant presentation by Feynman,³ who introduces mechanics following the route just described. Another hypothesis, which he immediately advances and was early noted by da Vinci,⁴ is that “there is no such thing as perpetual motion with weight lifting machines.” Feynman goes on to warn that “in fact, that there is no perpetual motion at all is a general statement of the law of conservation of energy.”

Newton’s laws allow us to identify the increase in the kinetic energy as the work done by the resultant or net force applied to a particle. Combining the concepts of gravitational potential energy and kinetic energy yields the principle of conservation of mechanical energy for a particle moving only under the effect of the gravitational force.

The generalization of these ideas to extended deformable bodies is at the origin of the notion of *internal energy*. A very simple example is depicted in Fig. 1(a). A pair of forces of the same magnitude and opposite directions acts on a body, deforming it. Clearly, there is work done by the forces, but the translational kinetic energy and the gravitational

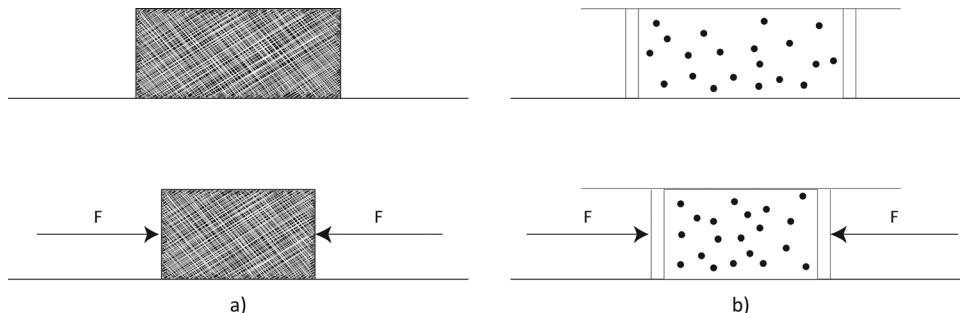


Fig. 1. A body deforms under the action of two forces of equal magnitude: (a) macroscopic picture; (b) microscopic picture, the body being an ideal gas in a container with movable walls.

potential energy of the body remain unchanged. This straightforward example also illustrates the power of the microscopic view. The simplest microscopic picture is to imagine the body as an ideal gas in a container with movable walls, Fig. 1(b). In this case, the work done is converted into kinetic energy of the constituents of the gas, which is the same as its internal energy.

With further maturation, this extension of the concepts of mechanics to deformable bodies is at the genesis of thermodynamics. Historically, however, thermodynamics evolved in a rather autonomous way. Its development was based on the concepts of heat and temperature, with properties apparently foreign to the phenomenology described by mechanics. These two new concepts were not easily encompassed by the formalism of mechanics, although there have always been “kinetic” conceptualizations of the thermodynamic quantities.⁵

The application of Newtonian physics to engineering, military engineering being of particular importance, forced mechanics to face the question of *friction*, which is always present in practice. Friction was—and still is—treated as a nonessential part of mechanics. One recurrent statement revealing the attempt to isolate mechanics from the phenomenology of friction is the claim that the equations of mechanics are reversible.

Friction brings to light that mechanics and thermodynamics are one and the same subject. The works of Maxwell and Boltzmann culminate an amazing effort of many authors to reconcile mechanics with thermodynamics, addressing the question of evolution to equilibrium. Boltzmann, in particular, proposing a microscopic interpretation of entropy,^{6,7} opens the door for a reevaluation of the meaning of several concepts, still problematic in the basic formulation of thermodynamics today.^{8,9} Let us pass through the door and travel this road in the remainder of this paper.

III. ENERGY AND ENTROPY: THE BASE MODEL

Thermodynamics has been established for a long time and there is a relatively consensual view on the way to present it. Most concepts, such as work, temperature, and heat, are introduced from the very beginning and in a very intuitive way. Nevertheless, various difficulties arise in the interpretation of fundamental quantities such as heat and work, even in simple situations. The subtleness of these seemingly simple and unambiguous notions leads to a search for consistency in the definitions of work and heat in the formulation of the first and second laws of thermodynamics, still very active today.^{10–20}

We suggest an early introduction of the variable entropy, postponing the appearance of the quantities temperature and

heat. This approach allows a formulation of thermodynamics that uses from the beginning the natural variables associated with the internal energy, which are the volume and the entropy. Moreover, all remaining quantities are introduced in a general and clear way, which, we believe, helps to prevent the misunderstanding and errors that spread even in the scientific literature. Finally, this procedure immediately provides an easily identifiable connection between mechanics and thermodynamics.

A. The need for the variable entropy

Thermodynamics can be introduced with generality from a clear, uncomplicated, “base model,” corresponding to one of the most typical systems in thermodynamics: a classical ideal gas in a container with a movable piston on top, under the action of gravity, as shown in Fig. 2. The system is surrounded by vacuum, so that there is no external atmospheric pressure on the piston. There is no friction between the piston and the container walls. Furthermore, it is assumed that the piston and the container walls do not have any internal structure, so that all collisions between the gas particles and the piston or the containing walls are perfectly elastic. This system can be studied starting only with the notions of

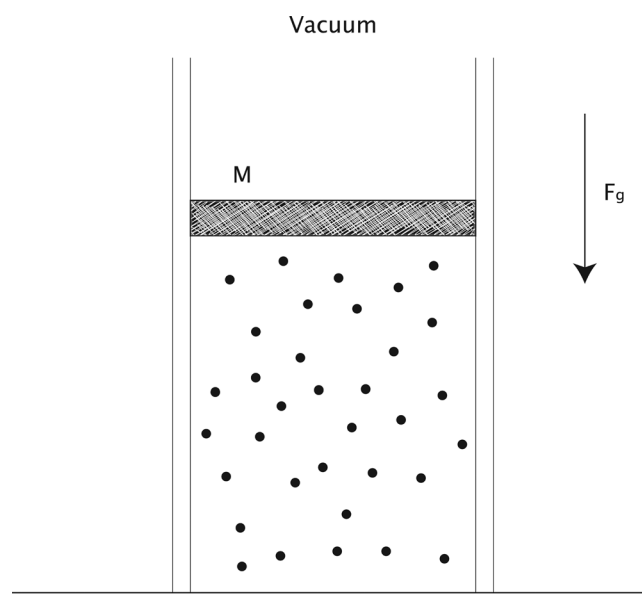


Fig. 2. The base model: An ideal gas is contained in a cylinder with a frictionless movable piston of mass M on the top.

weight, work done by the weight, gravitational potential energy, and internal energy. Note that a similar system was used by Kivelson and Oppenheim to discuss the concept of work in irreversible processes.²¹

Let us assume that the gas initially occupies a volume V_1 and exerts a pressure P_1 on the container walls. The piston is held fixed in its place. Its total mass, M , is such that the pressure exerted by the piston as soon as it is released,

$$P_e = \frac{Mg}{A} \quad (1)$$

is larger than P_1 , A denoting the area of the base of the piston.

The final equilibrium position of the piston can be determined if we know the dependence of the gas pressure on the gas internal energy. For a classical monoatomic ideal gas, from the microscopic picture and the calculation of the average momentum transfer per unit time, it is easy to show that this relation is

$$P = \frac{2U}{3V} = \alpha \frac{U}{V}, \quad (2)$$

where the value $\alpha = 2/3$ is specific to a monatomic gas, but other values of α can be used for diatomic and polyatomic gases, and even a relativistic gas of photons ($\alpha = 1/3$). As a matter of fact, for a container of dimensions $L \times L \times L$, a particle of mass m and speed v_x moving along the x direction hits one of the walls $v_x/2L$ times per unit time, and in each collision transfers a momentum $2mv_x$. Thus, the momentum transfer per unit time to the wall is mv_x^2/L . If we have N particles moving along the x direction and with different speeds, the average momentum transfer per unit time is $\langle \Delta p / \Delta t \rangle = Nm \langle v_x^2 \rangle / L$, where $\langle v_x^2 \rangle$ is the average value of v_x^2 . Further assuming that there is no privileged direction of motion, $\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = 3 \langle v_x^2 \rangle$. Finally, dividing by the area L^2 to obtain the pressure, we obtain

$$P = \frac{1}{L^2} \left\langle \frac{\Delta p}{\Delta t} \right\rangle = \frac{1}{3V} N m \langle v^2 \rangle, \quad (3)$$

which is Eq. (2) identifying the internal energy with the kinetic energy of the gas. Note that the potential energy of the gas particles is negligible compared to their kinetic energy. Furthermore, all the main results derived below do not depend on this approximation.

It is worth noting that, *despite the absence of friction, the piston does reach a final equilibrium position* and does not remain oscillating indefinitely. Or, more precisely, it will at first oscillate while slowly evolving to its equilibrium position and, once this position is reached, the piston stays *jiggling* around it. What happens is that the pressure exerted by the gas on the piston is a “dynamic pressure.”^{17–20} For the same volume, the dynamic pressure is higher in a compression and lower in an expansion.^{17–19} The piston moves under the action of the weight and of the dynamic force. Because of the imbalance between the two forces, the latter has a “dissipative character,” leading the piston to the final equilibrium position.¹⁸ The situation is somewhat similar to the case of a bullet entering at high speed in a region where there is a gas at room temperature. Even if all collisions between the gas particles and the bullet are perfectly elastic, the net effect is one of slowing down the bullet, until it finally stops. We will return to this point in Sec. V, where a one-dimensional

version of our base model, interesting as a model of thought and adequate for numeric simulations, is also suggested.

The final equilibrium position can be calculated from the principle of conservation of energy and the equality of the gas and piston pressures. The former implies that the decrease in the gravitational potential energy must correspond to an increase in the internal energy,

$$-Mg(h_2 - h_1) = U_2 - U_1, \quad (4)$$

where the indexes 1 and 2 refer to the initial and final states, respectively, and h is the height of the piston, $h = V/A$; the latter is the statement

$$\frac{Mg}{A} = \alpha \frac{U_2}{V_2}, \quad (5)$$

where Eq. (2) was used. We have as well

$$U_1 = \frac{P_1 V_1}{\alpha}, \quad (6)$$

so that

$$h_2 = h_1 \frac{\alpha}{1 + \alpha} \left(1 + \frac{P_1 A}{Mg\alpha} \right). \quad (7)$$

If $P_1 < P_e$, as we have assumed, then $h_2 < h_1$, as it should be. Nevertheless, Eq. (7) is valid for any relation between the initial gas pressures P_1 and P_e .

Let us now assume we remove a certain mass from the piston (for instance, we can imagine that the piston has several weights on the top of it, and we can simply remove one of them). The new total mass of the piston is $M' < M$ and the piston will reach a new equilibrium position, which we identify with the subscript 3. Let us look at the case where M' is such that the new equilibrium position, h_3 , is the same as the initial position h_1 . The energy conservation between positions 2 and 3 reads, similarly to Eq. (4),

$$-M'g(h_1 - h_2) = U_3 - U_2. \quad (8)$$

Therefore, combining this expression with Eq. (4), we arrive at the following very interesting result:

$$U_3 - U_1 = (M - M')g(h_1 - h_2) > 0. \quad (9)$$

Thus, when the piston goes back to its initial position, the internal energy of the gas is higher than it was initially. It is straightforward to show that this conclusion remains valid if initially we would have $P_1 > P_e$ and hence $h_2 > h_1$ and $M' > M$.

Equation (9) means that the internal energy cannot be solely a function of the volume, in contrast to the typical situations of mechanics (where the potential energy is only a function of position). If we assume that one further variable suffices to completely determine the internal energy, then we can write

$$U = U(V, S), \quad (10)$$

where the new variable, S , is called *entropy*.

B. Properties of entropy and the second law

Suppose now that the piston has initially a mass M_0 such that $AP_1/g = M_0$, which means that if the piston is released it stays at its equilibrium position. We can now add to the

piston a mass $m = (M - M_0)/2$ and wait for the piston to reach its new equilibrium position. Finally, we add yet another mass m to the piston, so that its total mass is M , as in the compression described in Sec. III A. Using the same reasoning as above, it is not difficult to show that the final equilibrium position corresponds to a position $h'_2 < h_2$. This, again, shows that the internal energy cannot be uniquely a function of the volume. Moreover, the lower height reached by the piston reflects the smaller imbalance between the dynamic force exerted by the gas and the weight, compared to the previous case.

We can further imagine a process in which the mass of the piston is increased in N equal steps from M_0 to M , for instance, by slowly adding sand grains, one by one, on the top of the piston. At each step, the dynamic force exerted by the gas is nearly the same as the weight. Therefore, the dissipative character of the dynamic force almost does not manifest itself. The piston reaches the lowest possible final position corresponding to a total mass M . Figure 3 illustrates this effect, by showing the final height of the piston as a function of the number N of masses $m = (M - M_0)/N$ added on the top of the piston. The calculations were carried out for $M_0 = 10$ kg, $M = 11$ kg, and $\alpha = 2/3$. The final height is plotted as a fraction of the initial height. The reader is invited to verify that the final result is given by

$$\frac{h_2}{h_1} = \prod_{k=1}^N \left[\frac{\alpha}{1+\alpha} + \frac{1}{1+\alpha} \frac{M_0 + (k-1)m}{M_0 + km} \right], \quad (11)$$

and that the limiting result is $(M_0/M)^{1/(1+\alpha)}$. For the case depicted in Fig. 3, we have $(10/11)^{3/5} \simeq 0.944418$.

Interestingly enough, if the sand grains are now slowly removed, one by one, we have again a near equilibrium between the dynamic force and the weight at all times. Everything nearly returns to the initial configuration and the gas will thus have very approximately the same internal energy as in the beginning. Figure 4 shows the final height h_3 as a function of masses used both during the compression and the expansion, normalised to the initial height h_1 .

Lastly, note that if we make the compression with a large number of steps, but the expansion quickly in few steps, we still find the need to add some additional mass to the piston to bring it to height h_1 and $U_3 > U_1$, as in Eq. (9). The same

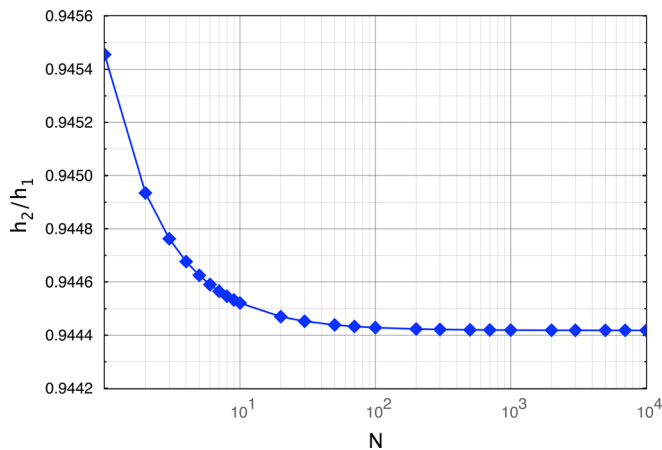


Fig. 3. Final equilibrium height of the piston after the compression, as a function of the number N of masses used to increase the total mass from $M_0 = 10$ kg to $M = 11$ kg (see text).

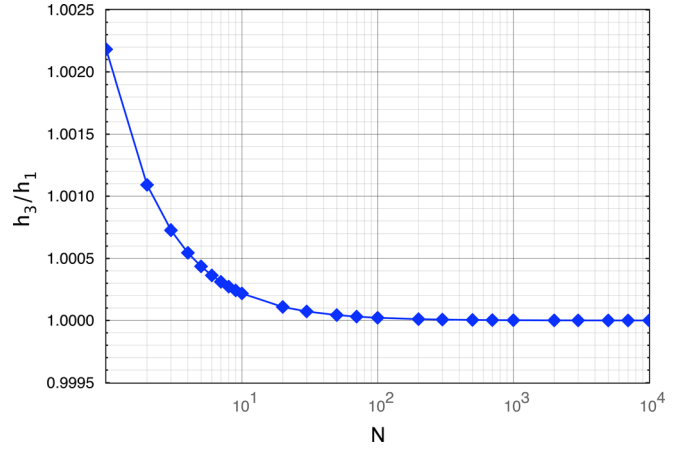


Fig. 4. Final equilibrium height of the piston after compression and expansion, as a function of the number N of masses used both to increase the total mass from $M_0 = 10$ kg to $M = 11$ kg and then to decrease it back to M_0 (see text).

happens if we do the expansion slowly with a large number of steps, but the compression with few steps.

Some properties of entropy can now be easily derived. Referring to this simple case treated with the base model, we have

$$U(V, S_3) \geq U(V, S_1). \quad (12)$$

If we arbitrarily postulate that $S_3 \geq S_1$, then *the entropy can only increase or remain constant*. Moreover,

$$\left(\frac{\partial U}{\partial S} \right)_V > 0. \quad (13)$$

Clearly, the situation with no entropy change corresponds to a *reversible* transformation, i.e., to a transformation where the initial state of the system can be recovered. In this case, the internal energy can be calculated only from the volume, as in the typical examples of mechanics. Thus, mechanics corresponds to *isentropic* thermodynamics, that is, to a set of transformations where the entropy does not change.

It is worth underlining two issues evidenced by the previous discussion and Figs. 3 and 4. The first one is that for deformable bodies (bodies with internal structure), the isentropic transformations can only be performed by *always* keeping the system nearly in equilibrium, when the dynamic force is always approximately balanced by the “static” weight force. Failing to do so, *either in the compression or the expansion*, or both, leads to an increase of the entropy and to the impossibility of recovering the initial state of the system. The latter statement exposes the second matter: it is not necessary to look at the complete sequence, compression plus expansion, to speak about a reversible transformation, as its reversible character, corresponding to constant entropy during the process, can be ascribed separately to the compression and to the expansion. In short, if a transformation leads from one state to a different one with the same entropy, then the transformation can be reversed, and vice-versa. The process just described of slowly adding or subtracting sand grains approaches the reversible ideal.

We have thus obtained the second law of thermodynamics, while keeping its interpretation and understanding at a very fundamental level. Evidently, in many situations studied in

mechanics, a variation of entropy does take place, although usually it is not taken into account. An example would be the treatment of the compression depicted in Fig. 1(a), considering the energy only as a function of the deformation. A similar case is the deformation of a spring and the application of Hooke's law. We will further discuss this point in Sec. V.

C. Introduction of the formalism

As shown in Secs. III A and III B, the internal energy depends (at least) on two variables, volume and entropy, as given by Eq. (10). Therefore, we can write

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS. \quad (14)$$

The idea of the increase in entropy as a result of the lack of balance between the dynamic and the static forces, advanced and discussed in Secs. III A and III B, can be confirmed as follows. The work of the resultant of the forces on the piston is equal to the variation of its kinetic energy. In differential form,

$$dE_{\text{kin}} = -\frac{Mg}{A} dV + \tilde{P} dV, \quad (15)$$

where \tilde{P} is the dynamic pressure exerted by the gas on the piston and dE_{kin} is the variation of the kinetic energy of the piston. On the other hand, the variation of the potential energy of the piston is

$$dE_{\text{pot}} = \frac{Mg}{A} dV. \quad (16)$$

Consequently,

$$dE_{\text{kin}} + dE_{\text{pot}} = \tilde{P} dV. \quad (17)$$

In addition, by conservation of energy,

$$dE_{\text{kin}} + dE_{\text{pot}} + dU = 0. \quad (18)$$

As a result,

$$dU = -\tilde{P} dV, \quad (19)$$

so that the variation of the internal energy of the gas is equal to the work done by the dynamic pressure.^{18–20}

Among the conclusions from Sec. III B, we have seen that a reversible transformation corresponds to a constant value of the entropy, so that $dS = 0$. What is more, the dynamic pressure is the same as the static pressure in this case. Hence, as $dU = -P_e dV$ and $P = P_e$, with P_e given by Eq. (1), from Eq. (14) we have

$$dU = -P_e dV = -P dV = \left(\frac{\partial U}{\partial V}\right)_S dV. \quad (20)$$

Thus, the quantity P can be defined from

$$P = -\left(\frac{\partial U}{\partial V}\right)_S, \quad (21)$$

which corresponds to the gas pressure for an equilibrium point.

Similarly, we can define the quantity T from

$$T = \left(\frac{\partial U}{\partial S}\right)_V > 0, \quad (22)$$

where the inequality is simply Eq. (13). It is not difficult to later identify T with the ideal gas temperature. This determination has been made by other authors.^{2,22} Notice, however, that, for an irreversible transformation, P and T are *defined* by Eqs. (21) and (22), respectively. In a dynamic situation, when the gas has a certain volume and a certain internal energy, P and T are the pressure and temperature *it would have if it were in equilibrium, with the same volume and internal energy*. This is the general meaning of P and T , and no other. Furthermore, in a dynamic situation P is *not* the pressure exerted by the gas. Naming P and T “pressure” and “temperature” and thinking in physical terms in these quantities, with these designations, as defined in equilibrium, is a common source of mistakes and misunderstandings.

Finally, we can write

$$dU = -\tilde{P} dV = -P dV + T dS \quad (23)$$

and

$$-(\tilde{P} - P) dV = T dS. \quad (24)$$

This last equation establishes that the variation of entropy is a consequence of the difference between the dynamic and the static pressures. This difference results in the “dissipative character” of the force, even if there is no friction, as pointed out and discussed in Sec. III A. This expression allows an additional verification that S always increases. As a matter of fact, if $dV > 0$ it must be true that $\tilde{P} < P$, so that $dS > 0$. The same conclusion is obtained if $dV < 0$, as then $\tilde{P} > P$.

To finish this section, let us go back to Eq. (19), to note that

$$\Delta U = -\int \tilde{P} dV, \quad (25)$$

which, denoting by W the work done by the dynamic force,

$$W = -\int \tilde{P} dV, \quad (26)$$

takes the expected form

$$\Delta U = W. \quad (27)$$

Moreover, it is immediate to verify that between two points where the piston is at rest the work done by the dynamic force W is equal to the work of the weight. Indeed, substituting Eq. (16) into Eq. (18), integrating and noting that in this case $\Delta E_{\text{kin}} = 0$,

$$\begin{aligned} \Delta U &= -\int \frac{Mg}{A} dV = -\int P_e dV \\ &= -\frac{Mg}{A} \Delta V = -\Delta E_{\text{pot}} = W. \end{aligned} \quad (28)$$

This consistency check does not constitute a surprise, as all our analysis of the base model started precisely from this condition. The interesting fact is that, despite $P_e \neq \tilde{P}$ along

the transformation, between two points where the piston is at rest we nevertheless have

$$\int P_e dV = \int \tilde{P} dV. \quad (29)$$

If the transformation is reversible, $dS=0$ along the transformation and, if the gas returns to the initial volume, using Eq. (23),

$$\Delta U = -\oint \tilde{P} dV = -\oint P dV = 0. \quad (30)$$

In general, for an irreversible transformation returning to the same volume,

$$\Delta U = -\oint \tilde{P} dV > 0. \quad (31)$$

Thus, the work of the dynamic force is transformed into internal energy, making the internal energy increase if the system returns to the initial volume, in accordance with the conclusions presented in Sec. III A.

In a generalization of the concept of heat,⁵ we can say that the work has been transformed into *heat*. Heat, however, is a subtle concept, still often misinterpreted (cf. Sec. IV C) and it would be better to rather say that “work has been used to heat the gas,” i.e., to increase its internal energy. Nonetheless, with the intuition acquired on the notion of variation of entropy associated with the base model, linking Newton’s second law with the second law of thermodynamics,¹⁸ we are now ready to infer the properties of more complex systems.

IV. HEAT: GENERALIZATIONS OF THE BASE MODEL

The natural generalization to a more elaborate configuration is a system comprised of two subsystems with a common boundary, through which they can exchange energy. We will consider various configurations. The first one consists of one subsystem of fixed volume and a second subsystem with a movable piston on top, leading to the formulation of the first law and the study of the heat reservoir. The second arrangement is the case of two subsystems side by side coupled by a moving piston, which allows the analysis of the celebrated “adiabatic piston” problem.^{3,19,20,23–25} A third geometry is the same as the previous one, but with the two subsystems arranged vertically. Finally, the last setup involves two subsystems side by side and a piston on the top of each of them, in order to study the constant pressure calorimeter.^{12,13}

A. Heat and the first law

The first geometry we want to investigate includes a subsystem *A* similar to the base model, namely, a classical ideal gas in a container with a moving piston. However, subsystem *A* is in now contact with another subsystem *B*, of fixed volume, as shown in Fig. 5. The *complete* system (formed by gases *A* and *B* and the piston) is isolated, but subsystems *A* and *B* can exchange energy with the piston and therefore the system (*A* + *B*) is not isolated. Furthermore, subsystems *A* and *B* can also change energy through the common border.

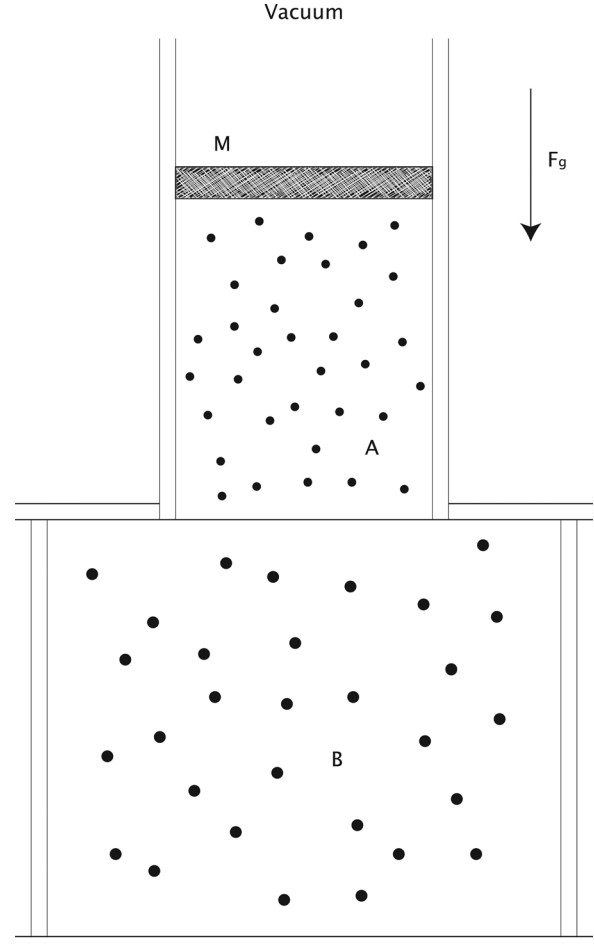


Fig. 5. Two subsystems, *A* and *B*, which can exchange energy through a common border. A frictionless piston of mass *M* can move and modify the volume of subsystem *A*.

The conclusions from our base model apply to the new system (*A* + *B*).

As the complete system is surrounded by vacuum, we have

$$U = U_A + U_B, \quad (32)$$

where *U* is the total internal energy, and *U_A* and *U_B* are the internal energies of subsystems *A* and *B*, respectively.

We can now write [cf. Eqs. (25) and (26)]

$$W = -\int \tilde{P} dV = \Delta U = \Delta U_A + \Delta U_B. \quad (33)$$

As before, between two points where the piston is at rest the work of the dynamic force is equal to the work of the weight. Rearranging this equation gives

$$\Delta U_A = W - \Delta U_B, \quad (34)$$

which we can put into a more familiar form by defining

$$Q = -\Delta U_B, \quad (35)$$

to obtain

$$\Delta U_A = W + Q. \quad (36)$$

This is the usual formulation of the first law of thermodynamics. (The symbol W is often defined with opposite sign, i.e., as the work done by the system, so that $\Delta U_A = Q - W$.) The quantity Q is called *heat* or heat exchanged with subsystem B . Its negative, $-Q$, is the change in the internal energy of subsystem B , or the energy transferred from A to B . The first law is thus a particular form of writing the principle of conservation of energy.

The introduction of heat in this simple but clear way gives a valuable contribution to help avoiding some of the most common traps related to this concept, as further discussed in Sec. IV C.

B. Temperature and the heat reservoir

One interesting result that can be easily obtained is the equality of temperatures of subsystems A and B described in Sec. IV A along reversible transformations. First note that, from Eq. (32),

$$dU = dU_A + dU_B. \quad (37)$$

Because U is a function of S and V , while $dS = 0$, we also have

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS - P dV = -P_A dV_A. \quad (38)$$

On the other hand,

$$dU_A = T_A dS_A - P_A dV_A, \quad (39)$$

and

$$dU_B = T_B dS_B, \quad (40)$$

where T_A and T_B are defined by Eq. (22). Combining these expressions, we obtain

$$T_A dS_A + T_B dS_B = 0. \quad (41)$$

Finally, assuming the entropy to be an extensive quantity (an assumption that can be motivated and discussed) and since the transformation is reversible,

$$dS = dS_A + dS_B = 0, \quad (42)$$

and hence, using Eq. (41),

$$T_A = T_B. \quad (43)$$

This shows that temperature characterizes the state of equilibrium of the two subsystems.

An important limiting case is where subsystem B is infinite, so that it constitutes a *heat reservoir*. Energy exchange with the smaller subsystem then does not change the temperature of reservoir B . This intuitive notion can be verified as follows. If the energy density is uniform, in each unit volume i of the heat reservoir we have the same volume V_i and the same internal energy U_i . Hence, since U_i is a function of S_i and V_i , all unit volumes have the same S_i . As the system is infinite, any finite transfer of energy will not change its energy per unit volume. Therefore, V_i , U_i , and S_i are not modified by a finite energy transfer to or from the heat reservoir. All quantities being the same, the derivatives (22) are

also the same and the temperature of the heat reservoir always remains unchanged. Equation (43) tells us that in this case a reversible transformation is an isothermal transformation at $T = T_B$. Moreover, since $dS_A = -dS_B$, using Eqs. (40) and (35),

$$dS_A = \frac{dQ}{T}. \quad (44)$$

C. The adiabatic piston

The so-called “adiabatic piston” problem concerns two ideal gases contained in a horizontal cylinder and separated by an *insulating piston that moves without friction*, as shown in Fig. 6. This system is more complex than the previous ones and has been treated by many authors.^{3,19,20,23–27} Worth noting are the qualitative kinetic description by Feynman,³ the molecular dynamics calculations by Mansour and co-workers,^{23,25} and the classical thermodynamics analysis by Gislason.¹⁹

Classical thermodynamics analyses are of major interest here. As pointed out in our previous work,²⁰ a careful use of thermodynamics must give the same final result as molecular dynamics, because the latter is a microscopic interpretation of the former. However, too commonly this is not the case, a fact that strikingly exemplifies the difficulties associated with the formalism of thermodynamics. Gislason gives a very interesting and enlightening discussion of the problem,¹⁹ focusing on the shorter time scale, when the two gases evolve to a situation of equal pressures. However, he does not address the second phase, when the gases evolve to a situation of equal temperatures, discussed qualitatively by Feynman³ and formally derived in our previous work.²⁰ On the other hand, Anacleto and Anacleto,²⁶ just to give one example, make a faulty investigation of the problem, claiming that the piston does not reach a final state of equilibrium, instead keeping oscillating indefinitely. Furthermore, they allege that entropy remains constant, due to the absence of friction, which is not the case.

The main difficulty with this problem arises from a negligent use of language. As a matter of fact, the word “adiabatic” is too swiftly associated with “no heat exchange” and is itself problematic. Moreover, “heat exchange” is rarely defined with generality, but we immediately are led to impose the mathematical condition $dQ = 0$ in the calculations.

The correct solution within the framework of thermodynamics was presented previously,^{20,24} and the reader should refer to those papers for the details on the formal use of the thermodynamic laws. Quoting from our former work,²⁰ by an “adiabatic piston” it is meant a piston *with zero heat conductivity*. If the piston is held in place (for instance, if it is

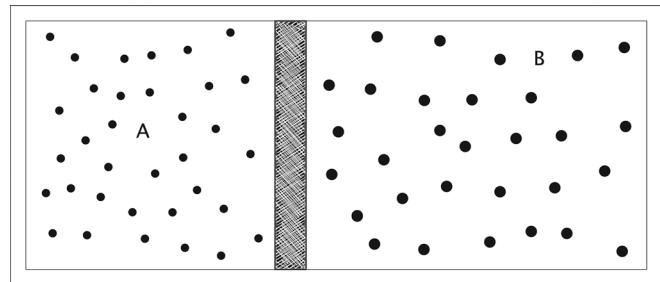


Fig. 6. Two subsystems, A and B , which can exchange energy through a moving “adiabatic” and frictionless piston.

fixed to the box by screws), then there is no “heat transfer” from one subsystem to the other. Even though, if the piston is released, both systems exchange energy via collisions with the piston, as they are coupled through the conditions of constant total volume and total energy, where the kinetic energy of the piston has to be taken into account. The evolution to a stage of mechanical equilibrium of equal pressures *has nothing to do with friction*: it is simply a result of the dissipative character of the dynamic pressure, discussed in our base model. There is indeed an entropy increase, as also acknowledged by Gislason in his analysis of the first phase of the problem.¹⁹ Gislason in fact provides significant physical insight by identifying the damping of the piston motion as a result of the dynamic pressure on it, “because the pressure is greater when the piston is moving towards the gas than when the piston is moving away from the gas.”¹⁹

After the equalization of pressures, the coupling between the two subsystems remains; only the kinetic energy of the piston becomes negligible. Still, the collisions between the gas particles and the piston will make the piston jiggle, allowing an exchange of energy between the two gases.^{3,20} These energy exchanges will always take place, despite the piston being a thermal nonconductor and the absence friction, as they are simply a result of the momentum transfer in the collisions (cf. the discussion by Feynman³). And, as pointed out in Sec. IV A, these energy exchanges can be formally treated as heat exchanges. Therefore, in this second phase, the system evolves to a situation of equal temperatures, with $\Delta U_A + \Delta U_B = 0$. In this case, if we write the first law for gas *A* we have $Q = -\Delta U_B \neq 0$ [Eq. (40)], and the condition $dQ = 0$ cannot be imposed.²⁰ In fact, we have instead $dQ_A = -dQ_B$ [Eq. (16) in Ref. 20]. Notice that the different quantities somewhat lose their intuitive interpretation, merely being a result of the mathematical formalism.

Another way of looking to the problem is to note that after the equalization of pressures, there are configurations in the vicinity of this mechanical equilibrium with greater global entropy, and the system will move towards these configurations. As a consequence, the system will indeed access the different available microscopic configurations and move as a result of a blind entropic process, in accordance with Boltzmann’s basic ideas and his microscopic interpretation of entropy. The latter also furnishes an explanation on the additive property of entropy.

From the discussion above, it is clear that during both phases of evolution there has to be a “heat exchange,” according to the formalism of thermodynamics, no matter whether the piston was defined as “adiabatic,” which might seem a bit shocking at first. The problematic use of language is easily avoided if we leave behind a formulation of the first law which to some extent still dates from the time of caloric, and instead keep in mind its introduction as suggested in Sec. IV A and from Eq. (35). Then, there is no doubt that the “adiabatic piston” system allows the energy exchange between both subsystems. And it is by no means shocking to assert that the internal energy of each subsystem changes due to the collisions, even for a piston with zero heat conductivity and moving without friction.

D. Further generalizations

From a general introduction of the first and second laws of thermodynamics and an early alert on the dangers of a blind use of the mathematical formalism, as outlined in

Secs. III–IV C, it is possible to proceed to more complicated and richer systems. This paper would become too lengthy if we would discuss them in detail here. Nevertheless, we will mention a few of them briefly.

1. The adiabatic piston in a gravitational field

A natural generalization is to consider the adiabatic piston from Sec. IV C, but now in a vertical configuration and under the effect of gravity. In this case, the work done by the dynamic force has two terms, one for the each gas. This case follows very closely the adiabatic piston discussed in our previous work.²⁰

The conservation of energy reads

$$dU_A + dU_B + dE_{\text{pot}} + dE_{\text{kin}} = 0, \quad (45)$$

where dU_A and dU_B are the internal energies of subsystems *A* (bottom) and *B* (top), respectively, whereas dE_{pot} and dE_{kin} are the piston gravitational potential energy and its kinetic energy, respectively. If the piston has mass M and area A , and noting that $dE_{\text{pot}} = (Mg/A)dV_A$, the reader is invited to adapt our former calculations²⁰ and verify that the equilibrium condition corresponds to equality of forces on the piston and equality of temperatures: $P_A = P_B + Mg/A$ and $T_A = T_B$.

Furthermore, since $dV_A + dV_B = 0$, the work of the resultant of the forces on the piston is [cf. Eq. (15)]

$$(\tilde{P}_A - \tilde{P}_B)dV_A - \frac{Mg}{A}dV_A = dE_{\text{kin}}. \quad (46)$$

Therefore, from Eqs. (45) and (46), we have

$$(\tilde{P}_A - \tilde{P}_B)dV_A = dE_{\text{kin}} + dE_{\text{pot}} = -dU_A - dU_B. \quad (47)$$

Finally,

$$\begin{aligned} \sum_i dU_i &= \sum_i (-\tilde{P}_i dV_i) \\ &= \sum_i (-P_i dV_i + T_i dS_i) \neq \sum_i (-P_i dV_i) \end{aligned} \quad (48)$$

with $i = \{A, B\}$, and

$$\sum_i T_i dS_i = - \sum_i (\tilde{P}_i - P_i) dV_i. \quad (49)$$

Exactly like the case of the adiabatic piston, the direct use of the first law for one of the gases and the assignment of physical meaning to the quantity Q are not straightforward, as neither the conditions $dQ = 0$ and $dU_i = -P_i dV_i$ nor even $dU_i = -\tilde{P}_i dV_i$ can be imposed.^{20,28}

2. The constant pressure calorimeter

One important configuration in practical applications is the constant pressure calorimeter.^{12,13} The system can be idealized by adding a piston to subsystem *B* from Fig. 5 to keep it at constant pressure. The new configuration is depicted in Fig. 7.

Let us denote the pressure exerted by the piston on subsystem *B* by P_0 . In other words, $P_0 = M_B g / A_B$, where M_B is the mass of the piston on subsystem *B* and A_B its area. Likewise, let us define $P_e = M_A g / A_A$.

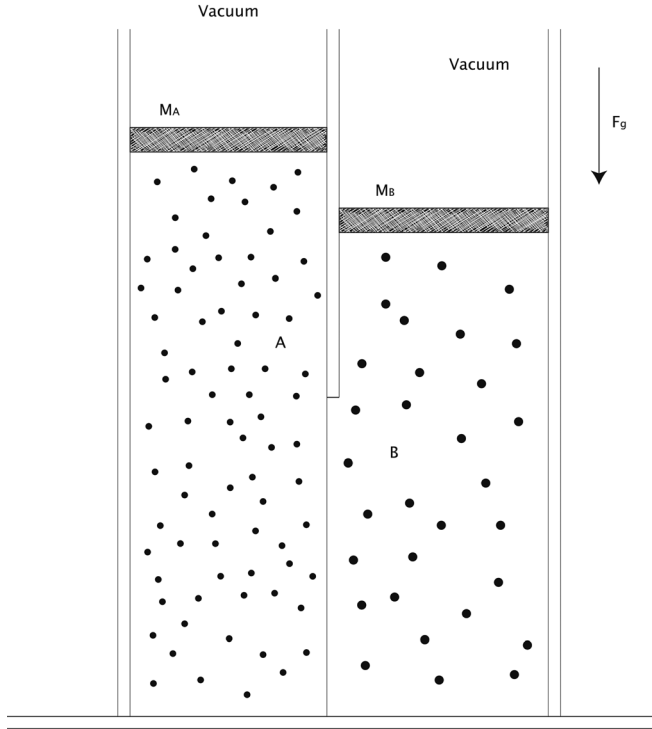


Fig. 7. The constant pressure calorimeter can be schematically represented by two subsystems, A (gas) and B (calorimeter), which can exchange energy through a common border. A frictionless piston of mass M_B keeps subsystem B at constant external pressure (instead of constant volume, as in Fig. 5).

Consider first a reversible transformation. In this case, the pressure P_B is always equilibrated at P_0 and there is no difference between P_B and \bar{P}_B . Therefore, defining the enthalpy H as

$$H = U + PV \quad (50)$$

and the specific heat at constant pressure C_P from

$$(dH)_P = C_P dT, \quad (51)$$

we have

$$\begin{aligned} dH_B &= d(U_B + P_B V_B) = dU_B + P_B dV_B = T_B dS_B \\ &\equiv C_{P,B} dT_B. \end{aligned} \quad (52)$$

To address the general case of an irreversible transformation (for instance, if we would initially have $P_e > P_A$), we note that the conservation of energy reads

$$dU_A + dU_B + dE_{\text{pot},A} + dE_{\text{kin},A} + dE_{\text{pot},B} + dE_{\text{kin},B} = 0, \quad (53)$$

where $dE_{\text{pot},A}$ and $dE_{\text{kin},A}$ are the potential and kinetic energies of piston A, given by Eqs. (15) and (16), respectively, and the same for piston B. Hence, we still have

$$dU_A + dU_B = -\tilde{P}_A dV_A - \tilde{P}_B dV_B. \quad (54)$$

Between two points where both pistons are at rest ($\Delta E_{\text{kin},A} = \Delta E_{\text{kin},B} = 0$) we have, successively,

$$\Delta U_A + \Delta U_B = -P_e \Delta V_A - P_0 \Delta V_B, \quad (55)$$

$$\begin{aligned} \Delta U_A &= -P_e \Delta V_A - (P_0 \Delta V_B + \Delta U_B) \\ &= -P_e \Delta V_A - \Delta H_B, \end{aligned} \quad (56)$$

where $\Delta H_B = \int C_{P,B} dT$. If the specific heat at constant pressure $C_{P,B}$ is constant, we can finally write

$$\Delta U_A = -P_e \Delta V_A - C_{P,B} \Delta T_B. \quad (57)$$

Thus, if we want to apply the first law of thermodynamics (36) to gas A, the second term on the r.h.s. corresponds to an energy exchange with subsystem B that we can identify with the heat exchanged with subsystem B between two points of equilibrium.

V. DISCUSSION

We have presented a simple and clear model for introducing thermodynamics, which reveals and naturally solves some of the difficulties underlying the concepts of work and heat in the formulation of the laws of thermodynamics.

The first step is the extension of the notions of kinetic and potential gravitational energies to the one of *internal energy*, inferred in Sec. II from the analysis of extended deformable bodies. Subsequently, from the base model presented in Sec. III it is shown that the internal energy depends on the position and entropy, $U = U(S, V)$.

It is pointed out that the *dynamic force* on the piston has a *dissipative character*, even if we have only conservative forces and there is no friction. The second law of thermodynamics is then readily obtained (Secs. III A and III B). An interesting idealized situation of our base model corresponds to a very simple one-dimensional picture, namely, a gas formed of N point particles of mass m moving only on the vertical direction under the action of gravity, and colliding elastically with the piston of mass M . There is no friction and the particles do not interact directly with each other. Even this straightforward model is enough to understand the dissipative character of the dynamic force, the approach to equilibrium, and, thus, irreversibility. In the case where all particles are initially exactly at the same height and have exactly the same velocity, the situation is the same as with a one-dimensional elastic collision between two point masses (one of mass Nm and the other of mass M). Therefore, the piston remains oscillating indefinitely. The dissipative character of the dynamic force does not appear and the entropy remains constant. The system “has no imagination,” the accessible volume in phase-space remaining very limited. However, if the masses m are not exactly “in phase,” if there is a small difference in their positions or speeds, the dissipative character emerges and there is an entropy increase (It can be noted that the notion of “exactly the same height and exactly the same velocity” does not make sense in quantum mechanics. However, it is not necessary to invoke quantum mechanics for the point we are making here). The accessible volume in phase-space has now increased. The key factor leading the evolution to equilibrium is the *interaction* between the different particles, even if it is kept to a minimum and only takes place indirectly through the collisions they experience with the piston. These ideas are in line with the pioneering works by Ludwig Boltzmann. A somewhat poetic statement expressing this main result would be “thermodynamics is mechanics with imagination.” A very interesting simulation of a rather similar system is available online from the NetLogo Models Library.^{29,30}

The approach to equilibrium raises the question of *irreversibility*. The example of compression/expansion with sand grains illustrates that the higher the imbalance between the dynamic and static pressures, the higher the increase in entropy, as also shown by Gislason.¹⁹ The importance of the so-called “quasi-static” formulations is then easily understood. It is the work of the dynamic force that is equal to the variation of the internal energy of the gas [Eq. (19)]. In a quasi-static process, the work of the dynamic force is a good approximation for the work of the static force during part of the trajectory of the piston, the variation of entropy being nearly zero [Eq. (24)]. For any real process, it is not possible to actually return to the initial conditions. Thus, it is necessary to generalize the idea of mechanical potential energy to the idea of gas internal energy. Whereas mechanical potential energy is a function of only the configuration (or deformation), here denoted V , the gas internal energy depends on one additional variable, S . Mechanics corresponds to isentropic thermodynamics, i.e., to situations where the internal energy is a potential energy, $U = U(V)$, either by the nature of the problem or as an approximation.

The traditional development of thermodynamics defines the internal energy first as a function of V and T . Noting that $(\partial U / \partial T)_V = C_V > 0$, we could then be led to think that mechanics corresponds to isothermal thermodynamics. However, this is not the case. During the sand-grain transformation of the base model, where $P \simeq P_0$, we have $dT \neq 0$. In particular, during the compression and the expansion we have, respectively, $dT > 0$ and $dT < 0$. The transformation is thus characterized by $dS = 0$ and not by $dT = 0$. That being so, mechanics indeed corresponds to isentropic thermodynamics and not to isothermal thermodynamics, reinforcing the importance of considering S the conjugate variable for V .

The idea that when a system returns to the initial position, such as after the compression–expansion from our base model, it has a higher internal energy than at the beginning [Eq. (9)], is fairly counterintuitive. This comes from the fact that physical systems are often surrounded by a thermostat, which prevents the manifestation of the thermodynamic phenomenon. A good example is the deformation of an elastic material, such as a spring hanging vertically, holding a certain mass. The situation is very much like our base model and an analysis similar to that in Sec. III A can be made. By way of illustration, a new mass can be added to the spring, which oscillates until a new equilibrium position is found. The additional mass can then be removed to the side and the spring again oscillates until it reaches its *original* equilibrium position, i.e., it recovers its initial deformation amount. We are led to think that everything happens as if the dynamic force could be approximated by the static force and internal dissipation would not exist, as *apparently* we return to the initial state. However, the excess internal energy and the entropy variation of the spring are transferred to the surrounding environment. The energy increase of the environment is equal to the work of the dynamic force and is equal to the changes of gravitational potential energy of the masses which are now at a lower level. Exactly the same would happen in the case of our base model in contact with a heat reservoir. This example strengthens the idea of using entropy as the additional variable, as an analysis based on the volume and temperature would hide the problem and we would be tempted to say that both the spring and the environment had recovered the initial state.

The heat reservoir was analyzed in Sec. IV B, as a limit of the case of energy exchanges between two subsystems, which can be described as *heat* exchanges. The first law, which should not be misinterpreted as a formal generalization of the principle of conservation of energy, is also derived in this context (Sec. IV A). Furthermore, the notion that “there is no such thing as perpetual motion with weight lifting machines”^{3,4} (Sec. II) can now be easily extended to account for the second law. In fact, this statement reflects the conservation of energy when entropy is not involved, so that $U = U(V)$. In this case, $W = \Delta U$ and, when the system returns to its initial position, $\Delta U = 0$ and hence $W = 0$. In the general case, with friction or even simply the reorganization of the internal energy as a result of the action of the dynamic force, $U = U(S, V)$, with $\Delta S > 0$. When the system returns to its initial position we have $\Delta U > 0$, so that $W > 0$, leading to the conclusion that “there is no perpetual motion at all.”³ This inference is valid both when subsystem B is finite (cf. Fig. 5) and in the limiting case of a heat reservoir, in what may be seen as a generalization of the Kelvin-Planck formulation of the second law.

The analysis of the adiabatic piston problem (Sec. IV C) has to be done with care. It is no longer possible to separate the energy-momentum exchanges of the particles from the two subsystems with the piston into quantities “work” and “heat” with clear energetic meaning. The correct and complete solution of this problem may contribute to illustrate the difficulty in assigning a physical meaning to these two quantities, as they appear in the laws of thermodynamics.^{20,24} The “jiggling piston” further provides a perfect bridge between thermodynamics and the microscopic structure of matter—Feynman’s *atomic hypothesis*, as he said to his students in the very first chapter of his *Lectures on Physics*.³ Although the final result of equal pressures and temperatures can be obtained without referring to heat and thermodynamics,³ the complete analysis allows a further exploration of the microscopic interpretation of entropy.³¹

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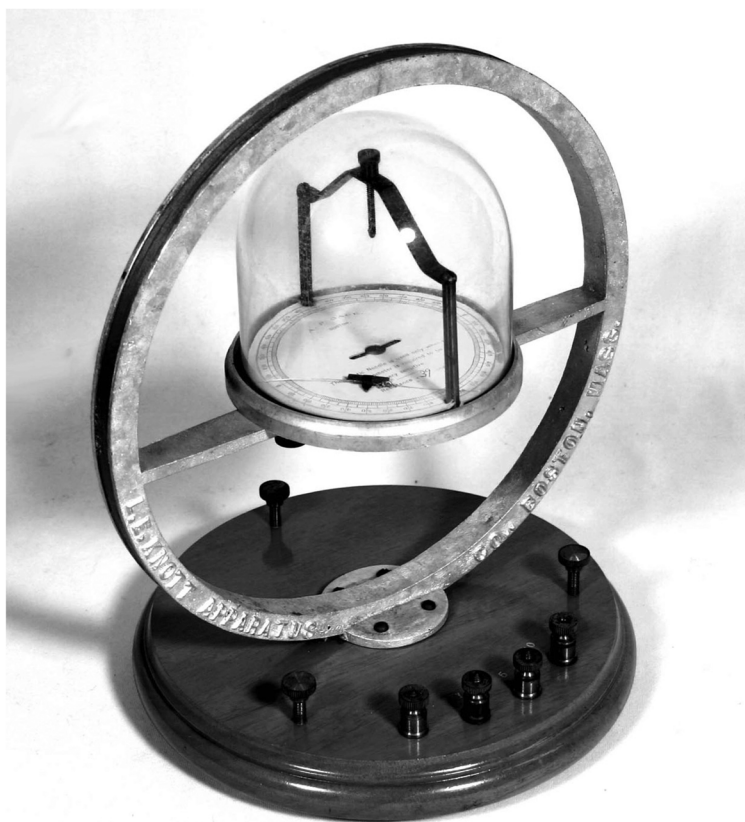
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Tangent Galvanometer. This "Harcourt Twenty-Two Centimeter Tangent Galvanometer" is listed at \$7.15 in the 1916 catalogue of the L.E. Knott Apparatus Company of Boston. The instrument is used with the coil oriented in the plane of the earth's magnetic field, and the galvanometer needle responds to the vector sum of the horizontal component of the earth's field and the field due to the coil. As is often the case, the suspension to the compass needle is broken. Note the early use of a large aluminum casting in the support ring for the coil. The instrument is in the Greenslade Collection. (Notes and photograph by Thomas B. Greenslade, Jr., Kenyon College)