

Introducing thermodynamics through energy and entropy

Rodrigo de Abreu and Vasco Guerra

Departamento de Física, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal

(Received 29 September 2011; accepted 12 March 2012)

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 American Association of Physics Teachers.

[<http://dx.doi.org/10.1119/1.3698160>]

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

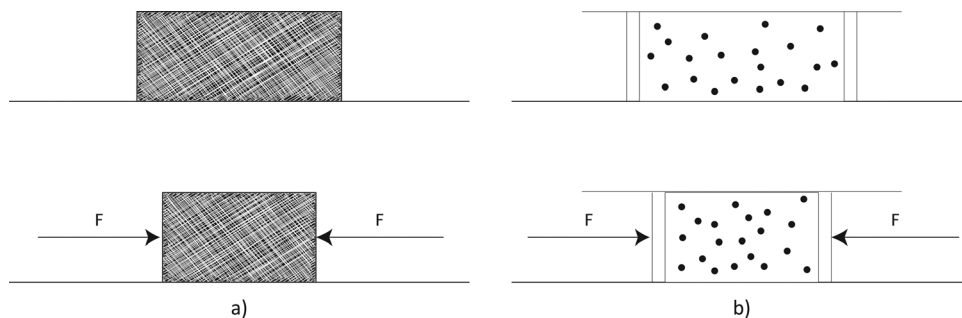


Fig. 1. A body deforms under the action of two forces of equal magnitude: (a) macroscopic picture; (b) microscopic picture, the body being an ideal gas in a container with movable walls.

96 potential energy of the body remain unchanged. This
 97 straightforward example also illustrates the power of the mi-
 98 croscopic view. The simplest microscopic picture is to imag-
 99 ine the body as an ideal gas in a container with movable
 100 walls, Fig. 1(b). In this case, the work done is converted into
 101 kinetic energy of the constituents of the gas, which is the
 102 same as its internal energy.

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

112 The application of Newtonian physics to engineering, mili-
 113 tary engineering being of particular importance, forced mechan-
 114 ics to face the question of *friction*, which is always present in
 115 practice. Friction was—and still is—treated as a nonessential
 116 part of mechanics. One recurrent statement revealing the
 117 attempt to isolate mechanics from the phenomenology of fric-
 118 tion is the claim that the equations of mechanics are reversible.

119 Friction brings to light that mechanics and thermodynam-
 120 ics are one and the same subject. The works of Maxwell and
 121 Boltzmann culminate an amazing effort of many authors to
 122 reconcile mechanics with thermodynamics, addressing the
 123 question of evolution to equilibrium. Boltzmann, in particu-
 124 lar, proposing a microscopic interpretation of entropy,^{6,7}
 125 opens the door for a reevaluation of the meaning of several
 126 concepts, still problematic in the basic formulation of ther-
 127 modynamics today.^{8,9} Let us pass through the door and travel
 128 this road in the remainder of this paper.

129 III. ENERGY AND ENTROPY: THE BASE MODEL

130 Thermodynamics has been established for a long time and
 131 there is a relatively consensual view on the way to present it.
 132 Most concepts, such as work, temperature, and heat, are
 133 introduced from the very beginning and in a very intuitive
 134 way. Nevertheless, various difficulties arise in the interpreta-
 135 tion of fundamental quantities such as heat and work, even
 136 in simple situations. The subtleness of these seemingly sim-
 137 ple and unambiguous notions leads to a search for consis-
 138 tency in the definitions of work and heat in the formulation
 139 of the first and second laws of thermodynamics, still very
 140 active today.^{10–20}

141 We suggest an early introduction of the variable entropy,
 142 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 en-
 tropy. 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 sci-
 entific literature. Finally, this procedure immediately provid-
 es 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 sur-
 rounded by vacuum, so that there is no external atmospheric
 pressure on the piston. There is no friction between the pis-
 ton 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

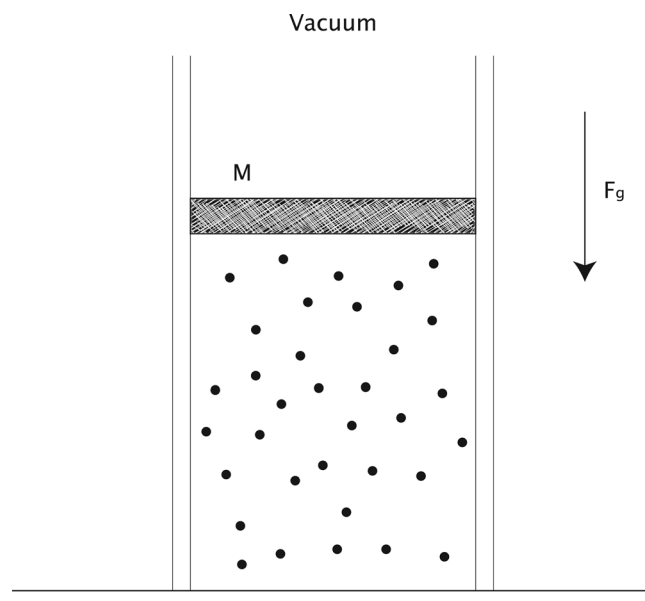


Fig. 2. The base model: An ideal gas is contained in a cylinder with a frictionless movable piston of mass M on the top.

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

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

271 We can further imagine a process in which the mass of the
 272 piston is increased in N equal steps from M_0 to M , for
 273 instance, by slowly adding sand grains, one by one, on the
 274 top of the piston. At each step, the dynamic force exerted by
 275 the gas is nearly the same as the weight. Therefore, the dissi-
 276 pative character of the dynamic force almost does not mani-
 277 fest itself. The piston reaches the lowest possible final
 278 position corresponding to a total mass M . Figure 3 illustrates
 279 this effect, by showing the final height of the piston as a
 280 function of the number N of masses $m = (M - M_0)/N$ added
 281 on the top of the piston. The calculations were carried out for
 282 $M_0 = 10$ kg, $M = 11$ kg, and $\alpha = 2/3$. The final height is
 283 plotted as a fraction of the initial height. The reader is invited
 284 to verify that the final result is given by

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

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

287 Interestingly enough, if the sand grains are now slowly
 288 removed, one by one, we have again a near equilibrium
 289 between the dynamic force and the weight at all times.
 290 Everything nearly returns to the initial configuration and the
 291 gas will thus have very approximately the same internal
 292 energy as in the beginning. Figure 4 shows the final height
 293 h'_3 as a function of masses used both during the compression
 294 and the expansion, normalised to the initial height h_1 .

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

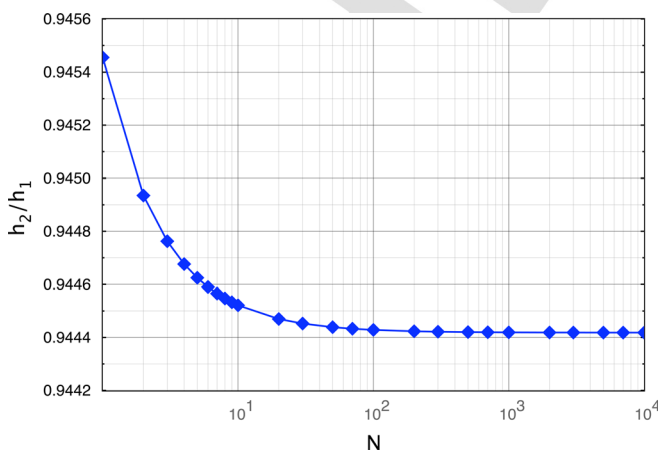


Fig. 3. Final equilibrium height of the piston after the compression, as a function of the number N of masses used to increase the total mass from $M_0 = 10$ kg to $M = 11$ kg (see text).

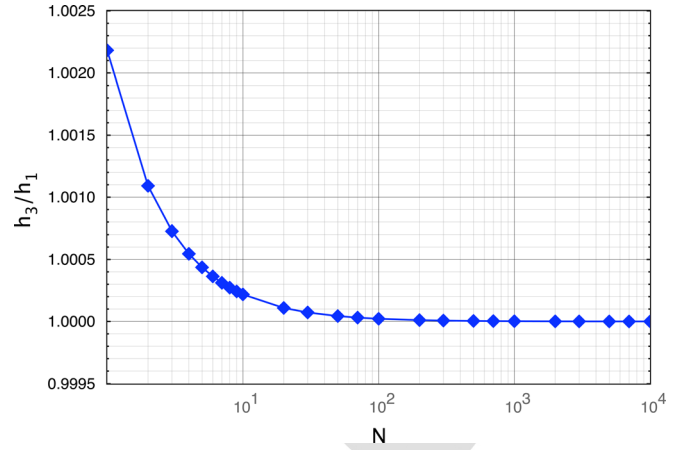


Fig. 4. Final equilibrium height of the piston after compression and expansion, as a function of the number N of masses used both to increase the total mass from $M_0 = 10$ kg to $M = 11$ kg and then to decrease it back to M_0 (see text).

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

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

341 C. Introduction of the formalism

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

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

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

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

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

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

355 Consequently,

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

356 In addition, by conservation of energy,

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

357 As a result,

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

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

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

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

366 Thus, the quantity P can be defined from

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

367 which corresponds to the gas pressure for an equilibrium
 368 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 determi-
 nation 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 in-
ternal 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 quanti-
 ties, with these designations, as defined in equilibrium, is a
 common source of mistakes and misunderstandings.

Finally, we can write

$$dU = -\tilde{P}dV = -PdV + TdS \quad (23)$$

and

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

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

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

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

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

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

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

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

413 Thus, the work of the dynamic force is transformed into in-
414 ternal energy, making the internal energy increase if the sys-
415 tem returns to the initial volume, in accordance with the
416 conclusions presented in Sec. III A.

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

427 IV. HEAT: GENERALIZATIONS OF THE BASE 428 MODEL

429 The natural generalization to a more elaborate configura-
430 tion is a system comprised of two subsystems with a com-
431 mon boundary, through which they can exchange energy.
432 We will consider various configurations. The first one cons-
433 ists of one subsystem of fixed volume and a second subsys-
434 tem with a movable piston on top, leading to the formulation
435 of the first law and the study of the heat reservoir. The sec-
436 ond arrangement is the case of two subsystems side by side
437 coupled by a moving piston, which allows the analysis of the
438 celebrated “adiabatic piston” problem.^{3,19,20,23–25} A third ge-
439 ometry is the same as the previous one, but with the two
440 subsystems arranged vertically. Finally, the last setup
441 involves two subsystems side by side and a piston on the top
442 of each of them, in order to study the constant pressure
443 calorimeter.^{12,13}

444 A. Heat and the first law

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

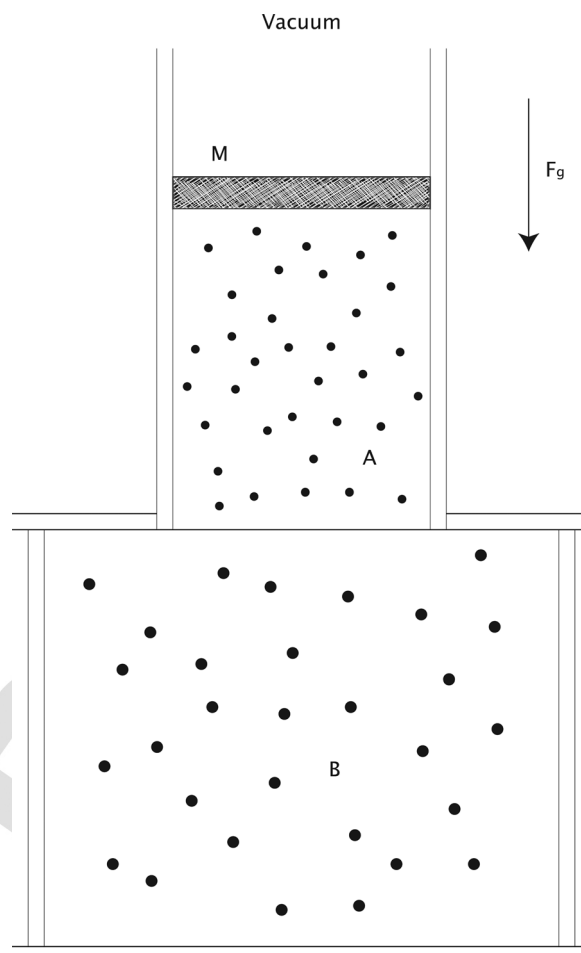


Fig. 5. Two subsystems, *A* and *B*, which can exchange energy through a common border. A frictionless piston of mass *M* can move and modify the volume of subsystem *A*.

The conclusions from our base model apply to the new sys- 454
tem (*A* + *B*). 455

As the complete system is surrounded by vacuum, we 456
have 457

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

where *U* is the total internal energy, and *U_A* and *U_B* are the 458
internal energies of subsystems *A* and *B*, respectively. 459

We can now write [cf. Eqs. (25) and (26)] 460

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

As before, between two points where the piston is at rest the 461
work of the dynamic force is equal to the work of the weight. 462
Rearranging this equation gives 463

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

which we can put into a more familiar form by defining 464

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

to obtain 465

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

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

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

478 B. Temperature and the heat reservoir

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

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

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

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

485 On the other hand,

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

486 and

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

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

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

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

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

492 and hence, using Eq. (41),

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

493 This shows that temperature characterizes the state of equi-
 494 librium of the two subsystems.

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

also the same and the temperature of the heat reservoir 507
 always remains unchanged. Equation (43) tells us that in this 508
 case a reversible transformation is an isothermal transforma- 509
 tion at $T = T_B$. Moreover, since $dS_A = -dS_B$, using Eqs. 510
 (40) and (35), 511

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

512 C. The adiabatic piston

The so-called “adiabatic piston” problem concerns two ideal 513
 gases contained in a horizontal cylinder and separated by an 514
insulating piston that moves without friction, as shown in Fig. 6. 515
 This system is more complex than the previous ones and has 516
 been treated by many authors.^{3,19,20,23–27} Worth noting are the 517
 qualitative kinetic description by Feynman,³ the molecular dyn- 518
 amics calculations by Mansour and co-workers,^{23,25} and the 519
 classical thermodynamics analysis by Gislason.¹⁹ 520

Classical thermodynamics analyses are of major interest 521
 here. As pointed out in our previous work,²⁰ a careful use of 522
 thermodynamics must give the same final result as molecular 523
 dynamics, because the latter is a microscopic interpretation 524
 of the former. However, too commonly this is not the case, a 525
 fact that strikingly exemplifies the difficulties associated 526
 with the formalism of thermodynamics. Gislason gives a 527
 very interesting and enlightening discussion of the prob- 528
 lem,¹⁹ focusing on the shorter time scale, when the two gases 529
 evolve to a situation of equal pressures. However, he does 530
 not address the second phase, when the gases evolve to a sit- 531
 uation of equal temperatures, discussed qualitatively by 532
 Feynman³ and formally derived in our previous work.²⁰ On 533
 the other hand, Anacleto and Anacleto,²⁶ just to give one 534
 example, make a faulty investigation of the problem, claim- 535
 ing that the piston does not reach a final state of equilibrium, 536
 instead keeping oscillating indefinitely. Furthermore, they 537
 allege that entropy remains constant, due to the absence of 538
 friction, which is not the case. 539

The main difficulty with this problem arises from a negli- 540
 gent use of language. As a matter of fact, the word “adiabatic” 541
 is too swiftly associated with “no heat exchange” and is itself 542
 problematic. Moreover, “heat exchange” is rarely defined 543
 with generality, but we immediately are led to impose the 544
 mathematical condition $dQ = 0$ in the calculations. 545

The correct solution within the framework of thermody- 546
 namics was presented previously,^{20,24} and the reader should 547
 refer to those papers for the details on the formal use of the 548
 thermodynamic laws. Quoting from our former work,²⁰ by 549
 an “adiabatic piston” it is meant a piston *with zero heat con-* 550
ductivity. If the piston is held in place (for instance, if it is 551

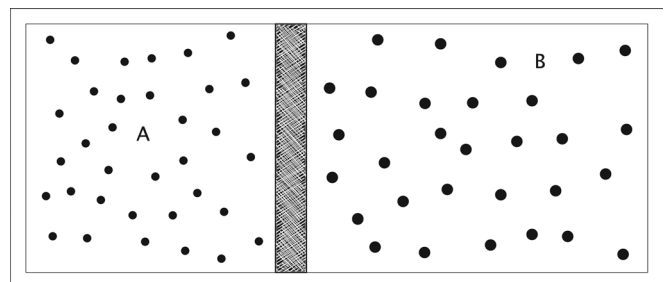


Fig. 6. Two subsystems, A and B , which can exchange energy through a moving “adiabatic” and frictionless piston.

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 $P_e = M_A g / A_A$.

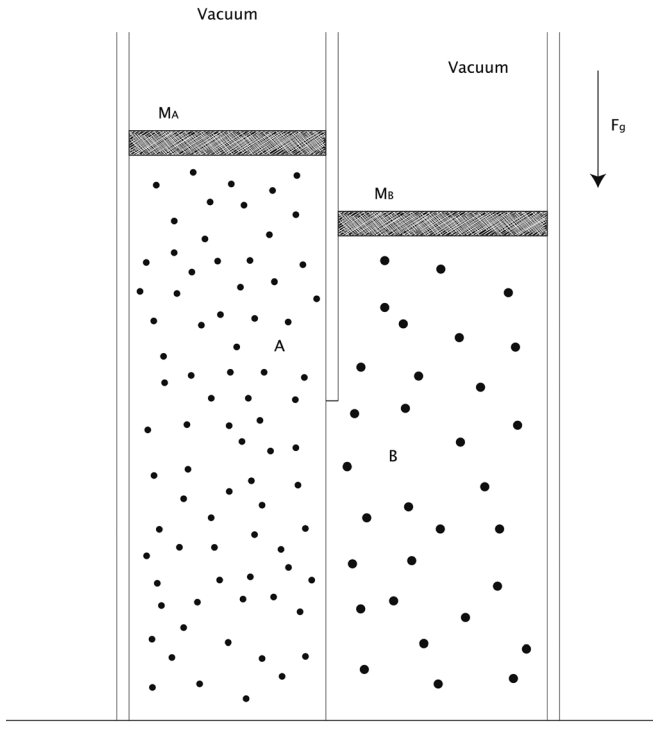


Fig. 7. The constant pressure calorimeter can be schematically represented by two subsystems, A (gas) and B (calorimeter), which can exchange energy through a common border. A frictionless piston of mass M_B keeps subsystem B at constant external pressure (instead of constant volume, as in Fig. 5).

655 Consider first a reversible transformation. In this case, the
 656 pressure P_B is always equilibrated at P_0 and there is no differ-
 657 ence between P_B and P_0 . Therefore, defining the enthalpy
 658 H as

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

659 and the specific heat at constant pressure C_P from

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

660 we have

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

661 To address the general case of an irreversible transforma-
 662 tion (for instance, if we would initially have $P_e > P_A$), we
 663 note that the conservation of energy reads

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

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

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

667 Between two points where both pistons are at rest
 668 ($\Delta E_{\text{kin},A} = \Delta E_{\text{kin},B} = 0$) 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 pres- 669
 670 sure $C_{P,B}$ 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 671
 (36) to gas A , the second term on the r.h.s. corresponds to an 672
 energy exchange with subsystem B that we can identify with 673
 the heat exchanged with subsystem B between two points of 674
 equilibrium. 675

V. DISCUSSION 676

We have presented a simple and clear model for introduc- 677
 ing thermodynamics, which reveals and naturally solves 678
 some of the difficulties underlying the concepts of work and 679
 heat in the formulation of the laws of thermodynamics. 680

The first step is the extension of the notions of kinetic and 681
 potential gravitational energies to the one of *internal energy*, 682
 inferred in Sec. II from the analysis of extended deformable 683
 bodies. Subsequently, from the base model presented in 684
 Sec. III it is shown that the internal energy depends on the 685
 position and entropy, $U = U(S, V)$. 686

It is pointed out that the *dynamic force* on the piston has a 687
dissipative character, even if we have only conservative 688
 forces and there is no friction. The second law of thermody- 689
 namics is then readily obtained (Secs. III A and III B). An 690
 interesting idealized situation of our base model corresponds 691
 to a very simple one-dimensional picture, namely, a gas 692
 formed of N point particles of mass m moving only on the 693
 vertical direction under the action of gravity, and colliding 694
 elastically with the piston of mass M . There is no friction 695
 and the particles do not interact directly with each other. 696
 Even this straightforward model is enough to understand the 697
 dissipative character of the dynamic force, the approach to 698
 equilibrium, and, thus, irreversibility. In the case where all 699
 particles are initially exactly at the same height and have 700
 exactly the same velocity, the situation is the same as with a 701
 one-dimensional elastic collision between two point masses 702
 (one of mass Nm and the other of mass M). Therefore, the 703
 piston remains oscillating indefinitely. The dissipative char- 704
 acter of the dynamic force does not appear and the entropy 705
 remains constant. The system “has no imagination,” the ac- 706
 cessible volume in phase-space remaining very limited. 707
 However, if the masses m are not exactly “in phase,” if there 708
 is a small difference in their positions or speeds, the dissipa- 709
 tive character emerges and there is an entropy increase (It 710
 can be noted that the notion of “exactly the same height and 711
 exactly the same velocity” does not make sense in quantum 712
 mechanics. However, it is not necessary to invoke quantum 713
 mechanics for the point we are making here). The accessible 714
 volume in phase-space has now increased. The key factor 715
 leading the evolution to equilibrium is the *interaction* 716
 between the different particles, even if it is kept to a mini- 717
 mum and only takes place indirectly through the collisions 718
 they experience with the piston. These ideas are in line with 719
 the pioneering works by Ludwig Boltzmann. A somewhat 720
 poetic statement expressing this main result would be 721
 “thermodynamics is mechanics with imagination.” A very 722
 interesting simulation of a rather similar system is available 723
 online from the NetLogo Models Library.^{29,30} 724

725 The approach to equilibrium raises the question of *irrever-*
 726 *sibility*. The example of compression/expansion with sand
 727 grains illustrates that the higher the imbalance between the
 728 dynamic and static pressures, the higher the increase in en-
 729 tropy, as also shown by Gislason.¹⁹ The importance of the
 730 so-called “quasi-static” formulations is then easily under-
 731 stood. It is the work of the dynamic force that is equal to the
 732 variation of the internal energy of the gas [Eq. (19)]. In a
 733 quasi-static process, the work of the dynamic force is a good
 734 approximation for the work of the static force during part of
 735 the trajectory of the piston, the variation of entropy being
 736 nearly zero [Eq. (24)]. For any real process, it is not possible
 737 to actually return to the initial conditions. Thus, it is neces-
 738 sary to generalize the idea of mechanical potential energy to
 739 the idea of gas internal energy. Whereas mechanical poten-
 740 tial energy is a function of only the configuration (or deforma-
 741 tion), here denoted V , the gas internal energy depends on
 742 one additional variable, S . Mechanics corresponds to isen-
 743 tropic thermodynamics, i.e., to situations where the internal
 744 energy is a potential energy, $U = U(V)$, either by the nature
 745 of the problem or as an approximation.

746 The traditional development of thermodynamics defines
 747 the internal energy first as a function of V and T . Noting
 748 that $(\partial U/\partial T)_V = C_V > 0$, we could then be led to think
 749 that mechanics corresponds to isothermal thermodynamics.
 750 However, this is not the case. During the sand-grain trans-
 751 formation of the base model, where $P \simeq P$, we have
 752 $dT \neq 0$. In particular, during the compression and the
 753 expansion we have, respectively, $dT > 0$ and $dT < 0$. The
 754 transformation is thus characterized by $dS = 0$ and not by
 755 $dT = 0$. That being so, mechanics indeed corresponds to
 756 isentropic thermodynamics and not to isothermal thermody-
 757 namics, reinforcing the importance of considering S the
 758 conjugate variable for V .

759 The idea that when a system returns to the initial position,
 760 such as after the compression–expansion from our base
 761 model, it has a higher internal energy than at the beginning
 762 [Eq. (9)], is fairly counterintuitive. This comes from the fact
 763 that physical systems are often surrounded by a thermostat,
 764 which prevents the manifestation of the thermodynamic phe-
 765 nomenon. A good example is the deformation of an elastic
 766 material, such as a spring hanging vertically, holding a cer-
 767 tain mass. The situation is very much like our base model
 768 and an analysis similar to that in Sec. III A can be made. By
 769 way of illustration, a new mass can be added to the spring,
 770 which oscillates until a new equilibrium position is found.
 771 The additional mass can then be removed to the side and the
 772 spring again oscillates until it reaches its *original* equilib-
 773 rium position, i.e., it recovers its initial deformation amount.
 774 We are led to think that everything happens as if the dynamic
 775 force could be approximated by the static force and internal
 776 dissipation would not exist, as *apparently* we return to the
 777 initial state. However, the excess internal energy and the en-
 778 tropy variation of the spring are transferred to the surround-
 779 ing environment. The energy increase of the environment is
 780 equal to the work of the dynamic force and is equal to the
 781 changes of gravitational potential energy of the masses
 782 which are now at a lower level. Exactly the same would hap-
 783 pen in the case of our base model in contact with a heat res-
 784 ervoir. This example strengthens the idea of using entropy as
 785 the additional variable, as an analysis based on the volume
 786 and temperature would hide the problem and we would be
 787 tempted to say that both the spring and the environment had
 788 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 generaliza-
 tion 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 reorganiza-
 tion 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 fi-
 nite (*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 com-
 plete solution of this problem may contribute to illustrate the
 difficulty in assigning a physical meaning to these two quan-
 tities, 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 micro-
 scopic interpretation of entropy.³¹

ACKNOWLEDGMENTS

The authors would like to thank the two anonymous refer-
 ees for their careful revision and many suggestions made,
 which decisively contributed to improve the clarity and
 enlarge the scope of the text.

¹K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1987).

²H. B. Callen, *Thermodynamics and An Introduction to Thermostatistics*, 2nd ed. (Wiley, New York, 1985).

³R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, 13th printing (Addison-Wesley, Reading, MA, 1979), Vol. I.

⁴L. da Vinci, “The Impossibility of Perpetual Motion,” In *Energy: Historical Development of the Concept (Benchmark Papers on Energy)*, edited by R. B. Lindsay (Hutchinson & Ross, Dowden, 1975), Vol. 1, p. 72.

⁵S. G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the Nineteenth Century, Book 1: Physics and the Atomists* (North-Holland, Amsterdam, 1986).

⁶L. Boltzmann, “Weitere studien über das wärme-gleichgewicht unter gasmolekülen,” *Wiener Berichte* **66**, 275–370 (1872).

⁷L. Boltzmann, “Über die beziehung dem zweiten Hauptsatze der mechanischen wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht,” *Wiener Berichte* **76**, 373–435 (1877).

⁸U. Besson, “The distinction between heat and work: An approach based on a classical mechanical model,” *Eur. J. Phys.* **24**, 245–252 (2003).

⁹J. M. Mínguez, “The work–energy theorem and the first law of thermodynamics,” *Int. J. Mech. Eng. Educ.* **33**, 77–82 (2005).

- 853 ¹⁰E. A. Gislason and N. C. Craig, "General definitions of work and heat in
854 thermodynamic processes," *J. Chem. Educ.* **64**, 660–668 (1987). 879
- 855 ¹¹G. M. Barrow, "Thermodynamics should be built on energy-not on heat
856 and work," *J. Chem. Educ.* **65**, 122–125 (1988). 880
- 857 ¹²E. A. Gislason and N. C. Craig, "Cementing the foundations of thermody-
858 namics: Comparison of system-based and surroundings-based definitions
859 of work and heat," *J. Chem. Thermodyn.* **37**, 954–966 (2005). 881
- 860 ¹³E. A. Gislason and N. C. Craig, "Pressure–volume integral expressions for
861 work in irreversible processes," *J. Chem. Educ.* **84**, 499–503 (2007). 882
- 862 ¹⁴S. G. Canagaratna, "Zeroth law, entropy, equilibrium, and all that,"
863 *J. Chem. Educ.* **85**, 732–736 (2008). 883
- 864 ¹⁵J. P. Bizarro, "Entropy production in irreversible processes with friction,"
865 *Phys. Rev. E* **78**, 021137 (2008). 884
- 866 ¹⁶J. P. Bizarro, "Thermodynamics with friction I. The Clausius inequality
867 revisited," *J. Appl. Phys.* **108**, 054907 (2010). 885
- 868 ¹⁷M. de Abreu Faro and R. de Abreu, "A One-Dimensional Model of Irre-
869 versibility," in *EPS 10 Trends in Physics (10th General Conference of the*
870 *European Physical Society)* (Sevilla, Spain, 1996), p. 314. 886
- 871 ¹⁸R. de Abreu, "Análise dinâmica da tendência para o equilíbrio num mod-
872 elo simples: a 2^a lei de Newton $f=ma$ e a 2^a lei da termodinâmica
873 $dS \geq 0$," (in Portuguese) (<http://arxiv.org/pdf/physics/0210084>) (2002). 887
- 874 ¹⁹E. A. Gislason, "A close examination of the motion of an adiabatic
875 piston," *Am. J. Phys.* **78**, 995–1001 (2010). 888
- 876 ²⁰R. de Abreu and V. Guerra, "Comment on 'A close examination of the
877 motion of an adiabatic piston,' by Eric A. Gislason [*Am. J. Phys.* **78** (10),
878 995–1001 (2010)]," *Am. J. Phys.* **79**, 684–685 (2011). 889
- ²¹D. Kivelson and I. Oppenheim, "Work in irreversible expansions,"
J. Chem. Educ. **43**, 233–235 (1966). 890
- ²²J. De Heer, *Phenomenological Thermodynamics with Applications to*
Chemistry (Prentice-Hall, Englewood Cliffs, NJ, 1986). 881
- ²³E. Kestemont, C. Van den Broeck, and M. Malek Mansour, "The 'adia-
883 batic' piston: and yet it moves," *Europhys. Lett.* **49**, 143–149 (2000). 884
- ²⁴R. de Abreu, "The first principle of thermodynamics and the non-
885 separability of the quantities 'work' and 'heat': The adiabatic piston con-
886 troversy," (<http://arxiv.org/abs/cond-mat/0205566>) (2002). 887
- ²⁵M. Malek Mansour, A. L. Garcia, and F. Baras, "Hydrodynamic descrip-
888 tion of the adiabatic piston," *Phys. Rev. E* **73**, 016121 (2006). 889
- ²⁶J. Anacleto and J. A. C. Anacleto, "Thermodynamical interactions: subtle-
890 ties of heat and work concepts," *Eur. J. Phys.* **29**, 555–566 (2008). 891
- ²⁷J. J. Brey and N. Khalil, "Critical behavior of two freely evolving granular
892 gases separated by an adiabatic piston," *Phys. Rev. E* **82**, 051301 (2010). 893
- ²⁸R. de Abreu and V. Guerra, "Comment on 'A close examination of the
894 motion of an adiabatic piston' by Eric A. Gislason [*Am. J. Phys.* **78**,
895 995–1001 (2010)]," (<http://arxiv.org/abs/1012.4918>) (2010). 896
- ²⁹U. Wilensky, Center for Connected Learning and Computer-Based Model-
897 ing, Northwestern University, Evanston, IL, ([http://ccl.northwestern.edu/](http://ccl.northwestern.edu/netlogo/models/GasLabAdiabaticPiston)
898 [netlogo/models/GasLabAdiabaticPiston](http://ccl.northwestern.edu/netlogo/models/GasLabAdiabaticPiston)) (1997). 899
- ³⁰U. Wilensky, Center for Connected Learning and Computer-Based Model-
900 ing, Northwestern University, Evanston, IL, ([http://ccl.northwestern.edu/](http://ccl.northwestern.edu/netlogo)
901 [netlogo](http://ccl.northwestern.edu/netlogo)) (1997). 902
- ³¹J. Arnaud, L. Chusseau, and F. Philippe, "Démocrite et la puissance
903 motrice du feu" (in french), (<http://arxiv.org/abs/1104.0836>) (2011). 904