

Deducing the 1st Law of Thermodynamics from the concept of Entropy



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Abstract

In the study of thermodynamics, the first law is usually presented after studies on temperature, heat and work. Here, we deduce the 1st law of thermodynamics from the concept of entropy. Although it is not normally treated this way, it is relevant to note how the laws of thermodynamics are interdependent. To proceed, we carried out a thorough bibliographic research, using deductive reasoning. The 1st law remains valid under the adopted perspective.

Keywords: 1st Law of Thermodynamics, Entropy, Physics Education, Dimensional analysis.

Resumen

En el estudio de la termodinámica, la primera ley suele presentarse tras estudios sobre temperatura, calor y trabajo. Aquí deducimos la primera ley de la termodinámica a partir del concepto de entropía. Aunque normalmente no se trata de esta manera, es relevante señalar cómo las leyes de la termodinámica son interdependientes. Para proceder, llevamos a cabo una exhaustiva investigación bibliográfica, utilizando un razonamiento deductivo. La primera ley sigue siendo válida bajo la perspectiva adoptada.

Palabras clave: 1ª Ley de la Termodinámica, Entropía, Educación Física, Análisis dimensional.

I. INTRODUCTION

We consistently cross paths with thermodynamics in daily life; we are surrounded by thermodynamic phenomena. The laws of thermodynamics are evident in automotive engineering, thermoelectric and thermonuclear power plants, heat engines, meteorology, and even the human body.

It is customary to study this part of physics in a hierarchical fashion; in particular, the 1st law follows studies on temperature, heat and work. Here, however, we carry out a mathematical deduction of the 1st law from the concept of entropy. We employ deductive reasoning, which, according to Gil [1, p.8], “starts from principles recognized as true and indisputable and makes it possible to reach conclusions in a purely formal way, that is, by virtue of its logic alone.”

II. ENTROPY AND THE 1ST LAW OF THERMODYNAMICS

Entropy is a measure of the irreversibility of physical processes. According to Callen [2] “... entropy S is a state property of the system; that is, it depends only on the state of the system and not on the way in which the system reaches that state” [p. 260]. The second law of thermodynamics is an extension of the existence of entropy, whereby the change in

entropy of the universe, after some process, increases or remains constant.

Thermodynamics understands entropy as a measure of the irreversibility of physical processes. Entropy can be defined by considering a thermodynamic process, which starts in a state I (initial) and reaches a final state F while exchanging matter and energy under the forms of heat and work with the surroundings. If such a process is reversible, it can be operated in reverse (FI) and the parameters will be preserved. But if such a process is irreversible, the reverse operation (F-I) will not be possible or, if possible, the amounts of matter and energy will be transformed and an irreversible loss will occur.

Mathematically, then, for a system that depends on the variables energy (E) and volume (V), Entropy (S) will be a function of both energy (E) and volume (V), $S = S(E, V)$, as follows [3]:

$$S(E, V) = k_b \log \Omega(E, V), \quad (1)$$

where k_b is Boltzmann's constant and is approximately $1.381 \times 10^{-23} \text{ J/K}^{-1}$ is the number of states with energy E , and the number of states is on the order of $\Omega(E) \sim e^N$. Thus, entropy is proportional to the number of particles in the system, $S \sim N$.

In a system with many particles, energy levels can be treated as a continuum. So when we consider that $\Omega(E)$ is the number of states with energy E , it means that $\Omega(E)$ has the

number of states with energy between E and $E + \delta E$, where δE is small. We analyze that as follows. Given “an isolated system in equilibrium, all accessible microstates are equally probable” [3, p. 4]. Then, it is reasonable to consider that all states have the same energy E , which is equivalent to all states being reachable by small perturbations in the system, i.e., the probability that the system is in an energy state other than E is zero ($E \neq E = 0$). This probability distribution, relevant for systems with fixed energy, is known as the microcanonical set [3], or “a statistical ensemble that represents the possible states of a mechanical system whose total energy is exactly specified.” [5]

The fact that entropy is proportional to the number of particles N in the system results in it being an additive quantity. Considering two systems that do not interact and have energies E_1 and E_2 , the total number of states of these systems is given by

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2), \quad (2)$$

and the entropy of the systems will be

$$S(E_1, E_2) = S_1(E_1) + S_2(E_2). \quad (3)$$

Considering the entropy of a composite system as a function of energy and volume, we have

$$S(E_1, V_1) = S_1(E_1, V_1) + S_2(E_2, V_2); \quad (4)$$

that is, it is extensive and means that all extensive features of the system are multiplied by a constant lambda λ , and entropy is multiplied by this same constant $S(\lambda E, \lambda V) = \lambda S(E, V)$ [4] as

$$S(\lambda E, \lambda V) = \lambda S(E, V), \quad (5)$$

$$S(\lambda E, \lambda V) = \frac{\partial S}{\partial(\lambda E)} \frac{\partial(\lambda E)}{\partial E} + \frac{\partial S}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial V}. \quad (6)$$

Since E and V do not depend on λ , we have the following relationship:

$$S(\lambda E, \lambda V) = \frac{\partial S}{\partial(\lambda E)} E + \frac{\partial S}{\partial(\lambda V)} V. \quad (7)$$

Equation (7) must hold for any value of λ ; making $\lambda = 1$, we have

$$S(E, V) = \frac{\partial S}{\partial E} E + \frac{\partial S}{\partial V} V. \quad (8)$$

In a differential form, we rewrite equation (8), as follows:

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \quad (9)$$

Using the statistical definition of temperature, we have

$$\frac{1}{T} = \frac{\partial S}{\partial E}. \quad (10)$$

The validity of equation (10) can be verified by dimensional analysis. By having $S = \left[\frac{\text{Joule}(J)}{\text{Kelvin}(K)} \right]$ e $E = [\text{Joule}]$, we will, in turn, have,

$$\frac{S}{E} = \left[\frac{J/K}{J} \right] = \left[\frac{1}{K} \right] = \frac{1}{T}. \quad (11)$$

In statistical physics, pressure is defined by equation (11).

$$p = T \frac{\partial S}{\partial V}. \quad (12)$$

Also using dimensional analysis, we can demonstrate the validity of equation (12). Considering $S = \left[\frac{\text{Joule}}{\text{Kelvin}} \right]$ e $V = [m^3]$, we have

$$T \cdot \frac{S}{V} = \left[K \cdot \frac{J/K}{m^3} \right] = \left[\frac{J}{m^3} \right]. \quad (13)$$

However, $J = \left[Kg \cdot \frac{m^2}{s^2} \right]$. Substituting the equivalent of Joule in the analysis, we will have

$$T \cdot \frac{S}{V} = \left[Kg \cdot \frac{m^2}{s^2} \cdot \frac{1}{m^3} \right] = \left[\frac{Kg}{s^2 \cdot m} \right], \quad (14)$$

and by the simplest definition, the pressure at a given point is the ratio of the force applied over a given area; that is, $p = \frac{F}{A}$, so

$$p = \left[\frac{N}{m^2} \right] = \left[\frac{Kg \cdot m/s^2}{m^2} \right] = \left[\frac{Kg}{s^2 \cdot m} \right], \quad (15)$$

which proves, by dimensional analysis, that: $p = T \frac{\partial S}{\partial V}$.

Returning to equation (9) for the second term, by equation (12), we will have

$$\frac{\partial S}{\partial V} = \frac{p}{T}. \quad (16)$$

Substituting into equation (9), equations (10) and (16), we have

$$dS = \frac{1}{T} dE + \frac{p}{T} dV,$$

$$dS = \frac{1}{T} (dE + p dV),$$

$$T dS = dE + p dV,$$

$$dE = T dS - p dV. \quad (17)$$

Using the relationship of entropy with heat transferred, we have the change of entropy dS , an exact differential, between two states, arising from the heat transferred $d'Q$, an inexact heat differential, divided by the system temperature T , as

$$dS = \frac{d'Q}{T}. \quad (18)$$

Substituting equation (18) into (17), we have

$$dE = T \frac{d'Q}{T} - p dV, \\ dE = d'Q - p dV, \quad (19)$$

where $p dV$ is the work done by the system $d'W$. Thus, we can rewrite equation (19) as

$$dE = d'Q - d'W. \quad (20)$$

The differences $d'Q$ and $d'W$ are inexact, as they do not represent variations of heat and work, respectively, between two states. They represent the dependence of such parameters on the thermodynamic process involved. For example, it is necessary to know whether the thermodynamic process is isobaric, adiabatic, isochoric or other in order to calculate the quantities $d'Q$ and $d'W$. On the other hand, the quantity dE is an exact differential, as it represents the variation of the internal energy of the system between two states (initial and final) and is independent of the thermodynamic process.

Equation (20) represents the 1st law of thermodynamics when a system undergoes an infinitesimal change in its state whereby a small amount of heat transfer and a small change in work take place.

The change in the internal energy of the system $\Delta E = E_f - E_i$ is equivalent to the change in the amount of heat absorbed by the system and the work done. Therefore, Equation (21) is the first law of thermodynamics for finite processes, or

$$\Delta E = \Delta Q - \Delta W. \quad (21)$$

We can conclude that equation (9) is a combination of the first and second principles of thermodynamics.

III. FINAL COMMENTS

While the 1st law of thermodynamics is typically based on temperature, heat, and work, we herein proposed a differentiated analysis of the 1st law through an unusual route: the concept of entropy. As determined through bibliographic research, this deduction is novel as it is not found in the Brazilian literature.

We used definitions of partial derivatives and the definitions of temperature and pressure and demonstrated from the concept of entropy that it is possible to deduce the first law of thermodynamics. This approach is relevant because in addition to clearly observing how the laws of thermodynamics are interdependent, it can be demonstrated that the 1st law remains valid under the adopted perspective. This demonstration allows us to observe that the quantities of the thermodynamic state (pressure, volume and temperature) are articulated in a manner independent of their analysis.

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