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Thermodynamics and Relativity: A Revised Interpretation of the Process of Gas Expansion

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Abstract: The gas expansion being among the basic processes examined in physics courses, its interpretation is generally considered as a well-known subject that does not need to be revisited. As explained in this paper, there is an ambiguity in the usual understanding of this simple process. The solution suggested consists in linking thermodynamics to relativity through the Einstein mass-energy relation.

Keywords: Thermodynamics, reversibility, irreversibility, energy, entropy, relativity, Einstein's relation

- 1 - Location of an ambiguity in the usual interpretation of the process of gas expansion

Let us consider an isolated system, having the form of a cylinder divided in two parts by a mobile piston. We suppose that, in the initial state, a gas is present in part 1, under the conditions V_i, P_i, T_i, while part 2 has been evacuated. If the piston, previously locked, is liberated, it moves towards the part of lower pressure, as a result of the expansion of the gas into the global system, where it reaches the final conditions V_f, P_f, T_f,.

This global system (part 1 + part 2) having been defined as isolated, if we apply to it the basic concepts of thermodynamics, we get a first series of relations that are generally written under the form:

$$dW_{syst} = - P_e \, dV_{syst} = 0 \tag{1}$$

(because the volume of the global system is fixed, implying $dV_{syst} = 0$)

$$dQ_{syst} = 0 \tag{2}$$

(because the wall of the global system is adiabatic)

Having:

$$dU_{syst} = dW_{syst} + dQ_{syst} \tag{3}$$

we get:

$$dU_{syst} = 0 \tag{4}$$

In the classical understanding of the first law, the equality $dU_{syst} = 0$ is considered as valid, whatever the level of irreversibility of the processes occurring inside the system. This proposition can itself be translated through the expression:

$$dU_{irr.syst} = dU_{rev.syst} = 0 \tag{5}$$

Despite the indisputable efficiency of the thermodynamic tool, the faith in eq. 5 presents an ambiguity that can be explained as follows.

Let us imagine an isolated system similar to the one considered above, but in which both parts contain a gas. In part 1, the initial conditions are P_{i1}, V_{i1}, T_{i1}, in part 2 they are P_{i2}, V_{i2}, T_{i2}. If the piston is liberated, it moves towards the part of lower pressure, until the pressures become equal.

In such a case, applying eq.1 to part 1 and part 2, gives:

$$dW_1 = - P_2^* dV_1 \tag{6}$$

$$dW_2 = - P_1^* dV_2 \tag{7}$$

where P_1^* and P_2^* represent the average values of P_1 and P_2 during the process.

Knowing that:

$$dV_2 = - dV_1 \tag{8}$$

we get:

$$dW_{syst} = dV_1(P_1^* - P_2^*) \tag{9}$$

Since dV_1 is positive when $P_1^* > P_2^*$ and negative when $P_1^* < P_2^*$, it appears that dW_{syst} is always positive, a proposition that can be noted:

$$dW_{syst} > 0 \tag{10}$$

Keeping in mind that the global system has been defined as isolated, the origin of this increase in mechanical energy is necessarily internal. The process previously evoked (expansion of gas into a vacuum) is nothing but a particular case of eq. 9, corresponding to the condition $P_2^* = 0$. For a given value of P_1^*, the case $P_2^* = 0$ is the one leading to the maximal value of dW_{syst}.

If we want to reconcile the result given by eq. 10 with the postulate expressed by eq. 4 and 5, we have to find, for the system taken in consideration, another kind of energy that would have a negative value.

Spontaneously we are tempted to think about heat and imagine that its variation must obey the condition:

$$dQ_{syst} < 0 \tag{11}$$

and more precisely:

$$dQ_{syst} = - dW_{syst} \tag{12}$$

The problem is that eq. 11 implies itself two possibilities. The first one is to imagine that the system loses heat that escapes towards the surroundings, but in such a case this system would not be isolated. The second possibility is in admitting that, within the system, an energy has disappeared by transformation in mass, but accepting this kind of hypothesis, we are leaving the field of conventional thermodynamics to enter the one of relativity.

- 2 - Suggested solution

The solution suggested here is evidently the one that takes into account the concept of relativity. For an easier presentation of the subject, the discussion can be divided in three steps.

a) **First step: Reversibility and Irreversibility in the case of work**.

As implicitly recalled in eq.1, the expression representing an irreversible process in the case of work is:

$$dW_{irr} = - P_e \, dV \qquad (13)$$

while the one representing a reversible process is:

$$dW_{rev} = - P_i \, dV \qquad (14)$$

For a given value of dV, the difference between dW_{irr} and dW_{rev} is therefore:

$$dW_{irr} - dW_{rev} = dV(P_i - P_e) \qquad (15)$$

that can equally be written:

$$dW_{irr} = dW_{rev} + dV(P_i - P_e) \qquad (16)$$

In eq. 15 and 16, the term $dV(P_i - P_e)$ is always positive (for the reason already seen with eq.9), so that another writing of this peculiarity is:

$$dW_{irr} = dW_{rev} + dW_{add} \qquad (17)$$

where dW_{add} represents an additional work, whose value is always positive.

b) **Second step: Reversibility and Irreversibility in the case of heat**.

This question is closely linked to the second law of thermodynamics which, in textbooks and courses, is often introduced through the formulation:

$$dS = dQ/T + dS_i \qquad (18)$$

whose precise significance is:

$$dS = dQ_{rev}/T_e + dS_i \qquad (19)$$

This equation has the dimension of an entropy but written under the form:

$$T_e dS = dQ_{rev} + T_e dS_i \qquad (20)$$

it takes the dimension of an energy.

Since dS_i is positive (fundamental information given by the second law) and T_e designates an absolute temperature, the term $T_e dS_i$ is itself positive. Therefore the physical significance of eq. 20 becomes:

$$dQ_{irr} = dQ_{rev} + dQ_{add} \qquad (21)$$

where dQ_{add} represents an additional energy, directly linked to the irreversibility, and having a positive value.

Observing that for an isolated system the term $dQ_{rev.syst}$ is zero, eq. 21 shows that the term $dQ_{irr.syst}$ is itself positive. As a consequence, the situation evoked by eq. 11 and 12 appears impossible, because it would be in contradiction with the second law.

c) Third step: Reversibility and Irreversibility in the general case of energy

Another point that can be noted is that eq. 21, which concerns heat, is similar to eq. 17, which concerns work. For this reason, both appear as particular forms of a more general energy equation that can be written:

$$dU_{irr} = dU_{rev} + dU_{add} \qquad (22)$$

When the thermodynamic system taken in consideration is isolated, the term dU_{add} of eq.22 is necessarily of internal origin, and the idea that comes in mind is the high probability of its correlation with the Einstein mass-energy relation $E = mc^2$. Taking into account that a decrease in mass leads to an increase in energy, and conversely, its differential can be written $dE = - c^2 dm$, giving to eq. 22 the significance:

$$dU_{irr} = dU_{rev} - c^2 dm \qquad (23)$$

Compared with the conventional presentation of the laws of thermodynamics, eq. 22 and 23 can be understood as follows.

- For the first law, the postulate $dU_{irr} = dU_{rev}$ is substituted by the postulate $dU_{irr} > dU_{rev}$. The difference corresponds to the term $dU_{add} = - c^2 dm$, whose value is zero in the case of a reversible process.

- For the second law, the concept of increase in entropy ($dS_i > 0$), classically associated to every irreversible process, is extended, and takes the dimension of an increase in energy ($dU_{add} > 0$)

The advantage is that both laws are gathered into a single formulation, with an opening between thermodynamics and relativity.

- 3 - Conclusions

The analysis presented above is a synthetic summary of the topics detailed in previous papers. Two of them are mentioned in the references quoted below [1, 2]. An important point concerns the fact that the hypothesis advanced is not a rejection of the thermodynamic theory but an extension, inspired by the idea that the Einstein mass-energy relation needs to be taken into account in the study of every irreversible process. Such a point of view was evidently unimaginable for the creators of the theory, since the concept of relativity was not known at that time.

- 4 - **Acknowledgments**

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In the books of thermodynamics for geologists quoted below [3, 4], I have greatly appreciated the comments of the authors - and of other great scientists - on their feeling that something seems not totally clear in the thermodynamic theory.

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