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Positive and negative entropy production in an ideal-gas expansion

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Abstract. – A theoretical thermodynamic analysis shows that an irreversible isothermal expansion of an ideal gas in a cylinder equipped with a piston may occur through trajectories involving a simultaneous positive and negative entropy production. Under these trajectories the operation is more efficient than a reversible expansion between the same initial and final states. This unexpected behavior may be explained as a consequence of an entropy coupling between the simultaneous positive and negative entropy production processes.

The motivation for this article is to illustrate the unusual behavior that a system may reach when it simultaneously produces and destroys entropy in different regions.

In this sense, we will analyze the irreversible expansion of an ideal gas operating under these conditions in a cylinder equipped with a piston without friction. Although the behavior described has not been observed experimentally in this simple model, this study may serve to increase insight in the theoretical investigations of this type of processes.

It should be cited that in some processes like thermal diffusion, coupled reactions, biological systems or in certain thermo mechanical systems, a simultaneous positive and negative entropy production [1–3] has been observed. For instance, in thermal diffusion, the heat flow kept by a temperature difference allows the diffusion of matter in a direction contrary to its concentration gradient, so that separation of a mixture is effected. Here, the heat flow produces enough positive entropy to compensate the negative entropy production of the transport of matter against its concentration gradient. These transitions may take place through an entropy coupling that connects the simultaneous positive and negative entropy production processes.

Since the main aspects of this article are related to the global and local formulation of the second law of thermodynamics and entropy coupling processes we will briefly discuss these topics.

The global formulation of the second law of thermodynamics postulates that for all possible processes the total entropy change of the universe that includes the system and its surroundings is equal to or greater than zero [1, 4, 5],

$$\Delta S_u = \Delta S_s + \Delta S_r \geq 0, \tag{1}$$

where ΔS_u, ΔS_s, ΔS_r represent the total entropy change of the universe, the entropy change of the system and the entropy change of the surroundings, respectively. In this equation, the equality holds for reversible processes and the inequality for irreversible transitions.

On the other hand, the local formulation of the second law of thermodynamics expresses that the entropy change of a system depends on the entropy flow due to exchanges with the surroundings and the entropy production due to changes inside the system [1,3],

$$\Delta S_s = \Delta S_e + \Delta S_i , \tag{2}$$

where ΔS_e, ΔS_i are the entropy flow and the entropy production, respectively. ΔS_i is equal to or greater than zero. It is zero when the system is subject to reversible processes, and positive if the system undergoes irreversible changes. The local formulation postulates that for a process involving several systems, the entropy production of each system, separately, including the surroundings, should be equal to or greater than zero in order to be possible. Although the local version of the second law prohibits the existence of a system where entropy production is negative, it may be possible to drive a negative entropy production system if we are able to couple this process with another one that produces enough positive entropy. At least two simultaneous processes are required to achieve this behavior, and one of the processes must produce sufficient positive entropy to compensate the negative entropy production. When this occurs an entropy coupling may take place allowing the existence of a system with simultaneous production and destruction of entropy. During the occurrence of an entropy coupling, the positive entropy production process allows to progress the negative entropy production process in a direction opposite to that given by its own nature [1].

Now, suppose we have a tank fitted with a piston and filled with 1 mol of a monatomic ideal gas initially at 300 K and 4 bar. The bottom of the tank is a good heat conducting metal which is placed in contact with a heat reservoir at 400 K. The lateral walls of the tank and the piston are well insulated to avoid thermal losses. Since the temperature of the heat reservoir is greater than the temperature of the ideal gas inside the tank, heat flows irreversibly from the reservoir to the ideal gas. During the process, the ideal gas receives heat from the hot reservoir and expands isothermally, doing work against an external pressure, reaching a final state at 300 K and 1 bar. To simplify calculations, it will be assumed that the piston and the walls of the tank are of negligible heat capacity and do not accumulate energy or entropy. Also, we neglect kinetic and potential energy changes.

By using the laws of thermodynamics, we will predict the work requirements for the above isothermal expansion operating under different trajectories. In order to apply the thermodynamics laws, the ideal gas enclosed in the cylinder may be considered as a closed system, surrounded by the heat reservoir at 400 K. Here, we will assume that the work W is positive when it is done by the system.

In our process, heat flows from the surroundings to the gas inside the tank, through a finite temperature gradient, then the transition is non-reversible, and work cannot be calculated by the following equation used for conventional reversible processes [4–7]:

$$W = \int P \, dV, \tag{3}$$

where P and V are the pressure and the volume of the gas, respectively. Instead of this equation, we will use a more general equation derived by combining the first law of thermodynamics and the global formulation of the second law of thermodynamics.

Since the ideal gas is exposed to an isothermal expansion, then the entropy change of the ideal gas ΔS_s is given by [3,4,6]

$$\Delta S_s = nR\ln(P_I/P_F), \tag{4}$$

where n, R, P_I and P_F are the number of moles, the gas constant, the initial gas pressure and the final gas pressure, respectively. R is equal to $8.314 \, \mathrm{J \, mol^{-1} K^{-1}}$.

Now, from refs. [4,6] the entropy change of the heat reservoir ΔS_r is

$$\Delta S_r = \int \mathrm{d}Q/T_r \tag{5}$$

here, Q is the heat transferred through the boundaries of the heat reservoir and T_r is the heat reservoir temperature. In this letter, we assume that Q is positive when it is added to a given system. Since heat flows from the heat reservoir to the ideal gas inside the tank, then Q is negative for the heat reservoir. Therefore

$$\Delta S_r = -Q/T_r \, . \tag{6}$$

Substituting eqs. (4) and (6) into eq. (1), we obtain

$$\Delta S_u = nR \ln(P_I/P_F) - Q/T_r \, . \tag{7}$$

From the first law of thermodynamics applied to a closed system neglecting kinetic and potential energy terms we get [4,6]

$$\Delta U = Q - W, \tag{8}$$

where ΔU is the internal energy change of the ideal gas. Since the ideal gas undergoes an isothermal process, then ΔU is zero [4,6]. Hence

$$Q = W. \tag{9}$$

By introducing eq. (9) into eq. (7), and solving for W we have

$$W = nRT_r \ln(P_I/P_F) - T_r \Delta S_u. \tag{10}$$

This equation allows us to estimate the work for any trajectory of an isothermal ideal-gas expansion, reversible or non-reversible.

For a reversible path, eq. (10) gives the same prediction as eq. (3) which is used for common reversible processes. In order to derive eq. (10) for the reversible case, we know [3–7] that a reversible process is constituted by a sequence of states that deviates infinitesimally from equilibrium, and in each stage, it can be turned into the reverse direction leaving the surroundings unmodified. The overall work of this cyclic process is zero. Similarly, the global heat exchanged with the surroundings during this cyclical process is also zero. Therefore, during a reversible process the system and the surroundings could be restored to their original states without producing any changes in the rest of the universe. This demands that the driving forces of the processes should be differential in size. In our case, this requires that the pressure and temperature differences between the system and the surroundings must be infinitesimal. According to these considerations, for a reversible isothermal expansion, the system temperature T should be infinitesimally less than the heat reservoir temperature T_r. Then, T_r tends to be equal to T for the reversible case, and eq. (10) becomes

$$W = nRT \ln(P_I/P_F) - T \Delta S_u \, . \tag{11}$$

For a reversible process the second law of thermodynamics indicates that the total entropy change of the universe ΔS_u is zero [3–6]. After introducing this requisite in eq. (11), we get the following expression for a reversible isothermal ideal-gas expansion

$$W = nRT \ln(P_I/P_F). \tag{12}$$

This equation coincides with the result that we obtain upon integration of eq. (3) for a reversible isothermal ideal-gas expansion. If the process described in this letter expands reversibly and isothermally from 4 to 1 bar at the system temperature of 300 K, then the work obtained from eq. (12) is 3457.70 J. According to classical thermodynamics, this is the maximum work that we can expect from the above isothermal expansion.

Now, considering the irreversible isothermal expansion specified in this letter, we can deduce, from eq. (10), that there are an infinite number of irreversible trajectories allowed by thermodynamic laws that may be used to carry out the proposed change of state. From this equation, we can estimate the work obtained for each one of the different irreversible trajectories that fits the thermodynamic requirements. Since ΔS_u must be greater than zero for each permitted irreversible path, we find by inspection of eq. (10), that the work allowed by thermodynamics laws should be equal to or less than 4610.26 J. By comparison, a common reversible expansion at 300 K, between the same initial and final states, produces 3457.70 J of work. Therefore, here, we have detected the theoretical existence of a set of non-conventional isothermal irreversible trajectories, allowed by thermodynamic laws, which produces more work than a reversible transition, between the same initial and final states. This is an unexpected performance not predicted by classical thermodynamics.

In order to get more insight about this uncommon behavior, we can express the work W in terms of the production of entropy using eq. (2). In agreement with this equation, the entropy change of the ideal gas ΔS_s is equal to the entropy flow due to the exchanges with the surroundings ΔS_e plus the entropy production of the ideal gas ΔS_{ig}. In our case, the system constituted by the ideal gas only exchanges heat with the surroundings, then from ref. [1], the entropy flow is given by

$$\Delta S_e = \int dQ/T\,, \tag{13}$$

where T is the absolute temperature of the ideal gas, and Q is the heat transferred to the ideal gas from the surroundings; then

$$\Delta S_e = Q/T\,. \tag{14}$$

Substituting eq. (14) into eq. (2), we find

$$\Delta S_s = Q/T + \Delta S_{ig}\,. \tag{15}$$

Combining eq. (4) and eq. (15), and solving for ΔS_{ig} we get

$$\Delta S_{ig} = nR\ln(P_I/P_F) - Q/T\,. \tag{16}$$

Now, substitution of eq. (6) and eq. (15) into eq. (1) gives

$$\Delta S_u = \Delta S_{ig} + Q(1/T - 1/T_r). \tag{17}$$

From ref. [1], the term $Q(1/T-1/T_r)$ represents the production of entropy due to the heat flow from the surroundings to the ideal gas inside the tank ΔS_{im}. Thus

$$\Delta S_{im} = Q(1/T - 1/T_r) \tag{18}$$

and

$$\Delta S_u = \Delta S_{ig} + \Delta S_{im}\,. \tag{19}$$

This equation indicates that the total entropy change of the universe ΔS_u is equal to the entropy production of the ideal-gas expansion ΔS_{ig} plus the entropy production due to the heat flow from the heat reservoir to the ideal gas inside the tank ΔS_{im}.

Then, substituting eq. (19) into eq. (10), we can express W in terms of the production of entropy ΔS_{ig} and ΔS_{im},

$$W = nRT_r \ln(P_I/P_F) - T_r(\Delta S_{ig} + \Delta S_{im}). \tag{20}$$

According to eq. (20), the work decreases if the entropy production terms are positive, and the work increases if these terms are negative. In other words, a positive entropy production decreases the ability of the system to do mechanical work, but a negative entropy production enhances the capacity to do work.

By inspection of eqs. (16), (18) and (19), we detect that those non-reversible isothermal trajectories where the total entropy change of the universe ΔS_u is greater than zero, and the entropy production terms ΔS_{ig} and ΔS_{im} are positive, produce work lower than 3457.70 J. These trajectories are permitted by the second law of thermodynamics, and coincide with conventional paths allowed by classical thermodynamics. Since the actual work of the process is less than the reversible work, then some work is lost, with respect to the work that the system would have done, if the process had been carried out reversibly. It may be suggested that a part of the reversible work is lost because of the production or "creation" of entropy in all regions of the universe [5], which decreases the capacity of the system to do mechanical work.

On the other hand, those non-reversible isothermal trajectories that produce work greater than 3457.70 J and lower than 4610.26 J, involve paths with positive and negative entropy production terms, and are allowed by the global formulation of the second law of thermodynamics, because the total entropy change of the universe ΔS_u is greater than zero. Here, the positive entropy production due to heat flow from the hot reservoir to the ideal gas inside the tank ΔS_{im}, compensates the simultaneous negative entropy production of the ideal-gas expansion ΔS_{ig}, and $\Delta S_{im} > \Delta S_{ig}$. In this region of positive and negative entropy production, the actual work produced by the system is greater than the reversible work between the same initial and final states. It may be suggested that because of the negative entropy production taking place during the ideal-gas expansion, some work is gained by reason of the "destruction" or "absorption" of entropy, increasing the capacity of the system to do work. It may be proposed that an entropy coupling takes place, driving the process according to thermodynamic expectations. I would like to stress that these trajectories fit the general thermodynamic laws, in the sense that the total energy of the process is conserved and that the total entropy change of the universe is greater than zero. Evidently, these trajectories do not follow the classical thermodynamic behavior that asserts the optimality of reversible changes or the principle that proposes that a reversible expansion yields the maximum possible work. In contrast, these findings suggest that non-reversible processes can be more optimal than reversible ones, a general fact known, in principle, from previous studies [8,9].

Although the statement of the problems in refs. [8,9] differ from the one considered in this paper, it is interesting to discuss these works, because the authors obtain the same general result described in this letter, suggesting that non-reversible processes can be more optimal than reversible ones. In this sense, ref. [8] discusses the operation of cyclic and non-cyclic processes at faster pumping rates and faster relaxation of the working fluid than in the case of reversible operation. They find that these processes are more efficient than reversible ones when both an irreversible entropy production and an entropy increase of the working fluid are allowed. In relation to ref. [9], the authors describe a situation where the direct interaction between the baths of a heat engine enhances its efficiency beyond the classical limits. The

study shows that, in a certain time window, the direct interaction between two systems at different temperatures may have useful energy transfer rather than energy dissipation. Since the time scale of the valuable energy transfer can be broadly separated from the time scale of the energy dissipation process, then an optimization of the conventional heat engine, in some time window, may be achieved, because the system relaxes to a different final state.

In conclusion, the thermodynamic approach presented in this letter predicts the theoretical existence of an infinite set of trajectories involving a simultaneous positive and negative entropy production in an irreversible isothermal ideal-gas expansion. These non-reversible trajectories are more efficient than the corresponding reversible path between the same initial and final states, and may take place through an entropy coupling process allowed by thermodynamic laws.

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