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Artículo Científico

On the misuse of Prigogine's Global Formulation of the Second Law and the Prediction of Negative Entropy Production in Macroscopic Irreversible Processes

Pedro J. Colmenares

Quimicofísica de Fluidos y Fenómenos Interfaciales (QUIFFIS)
Departamento de Química. Universidad de los Andes, Mérida 5101, Venezuela

colmenar@ula.ve

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Resumen

Este artículo presenta argumentos termodinámicos y mecánico estadísticos para demostrar la imposibilidad de una propuesta[1], en que una combinación de procesos de producción y destrucción de entropía, podría explicar el por qué es posible realizar más trabajo en un proceso irreversible que en uno reversible entre los mismos estados inicial y final. Se clarifican los errores termodinámicos y se proporciona evidencia teórica y experimental[2] de que a nivel macroscópico, la propuesta en cuestión no tiene oportunidad de ser observada fenomenológicamente debido a las restricciones impuestas por la Segunda Ley de la Termodinámica.

Palabras claves: Irreversibilidad; producción de entropía.

Abstract

This article presents thermodynamic and statistical mechanics arguments to proof the impossibility of a proposal[1] in which the interplay of production and destruction entropy processes would explain why it is possible to do work more efficiently in an irreversible process than in a reversible one between the same initial and final states. We clarify all the thermodynamic misleading and, provide theoretical and experimental evidence[2] that, a macroscopic level of description, the proposal has no chance of being observed phenomenologically because of the restrictions imposed by the second law of thermodynamics.

Key words: Irreversibility; entropy production.

I. Motivation

There have been many attempts to subvert the second law. Fortunately we dispose of powerful tools, such as the Irreversible Thermodynamics formalism (ITF), which provides the understanding of many phenomena, which at first sight, seem to contradict the law of physics. Thus, phenomena as thermal diffusion, also called the Soret effect in liquids, i.e., the parallel or antiparallel flow of matter due to a temperature gradient, or its reciprocal, the Dufour effect, to cite few among them, have been completely understood by assuming that the process itself is not the single combination of separated and independent processes, but a sophisticated one, composed by their interference to give rise a cross effect, which as a whole, overwhelmingly surpass any violating second law process occurring in the system. The theoretical framework on which these natural phenomena are fully understood, is the pioneer work of Lars Onsager, and later refined by Casimir, through their well-known theory of phenomenological coefficients and reciprocal relations[3-5].

Although ITF is, in general, the most suitable tool to analyze irreversible processes, there are many of them, which because of their simplicity, can be fully understood by means of classical thermodynamics. However, being the thermodynamics clear and precise on the predictions of the phenomenological measurements, any erroneous interpretation of it necessarily leads, among others, to a conclusion that the ubiquitous second law can be violated.

This is the case of the well-known book problem posed in ref. 1 of the irreversible heat transfer from a reservoir to an ideal gas enclosed in a vessel. There, it is predicted the existence of an ad hoc set of irreversible processes that jointly produce work greater than the reversible one, between the same initial and final states, due to the existence of an obscure mechanism of entropy production and destruction processes in which the latter overpass the former. As we will show, this unphysical coupling, which shares a similar conclusion as one proposed in 1993[6], is based on the misinterpretation of Prigogine's global formulation of the thermodynamic second principle that explicitly prohibits the destruction of entropy in one part of a macroscopic system[7]. As it was proved elsewhere[6], one of the reasons for which the 1993 proposal failed in the overthrow of the second principle was, besides an unphysical mechanical premise, the erroneous assumption that entropy production is an extensive property in the pure thermodynamic sense. In the proposal matter of this clarifying note, the problem lies again on the incorrect mechanical interpretation of the classical thermodynamic equations of the system. Furthermore, it is incorrectly assumed in ref. 1 that the obtained scheme, shares similarities with the results of an investigation in the quantum regime[8] [8], without been aware that within this level of description, the thermodynamic limit does not hold.

The aim of this comment note is to show that the second law does not allow those processes. Firstly, it will be point out the mistakes incurred in the proposal[1] on the correct interpretation of the equations provided by the thermodynamics of the problem under consideration and, secondly, it will be presented a short review on the statistical mechanics analysis about second law violating processes and the experimental evidence that the pre-cited law, as it should be, does not hold at the microscopic level of description.

II. Prigogine Statement of the Second Law

Quoting Prigogine[7]:

The second principle of thermodynamics postulates the existence of a function of state, called entropy, which possesses the following properties:

- *The entropy of the system is an extensive property.*
- *The change of entropy dS can be split into two parts. Denoting by d_eS the flow of entropy, due to interaction with the exterior, and by d_iS, the contribution due to changes inside the system, we have*

$$dS = d_eS + d_iS \qquad (1)$$

The entropy increase d_iS, due to changes inside the system, is never negative.

It is zero when the system undergoes reversible changes only, but it is positive if the system is subject (sic) to irreversible processes as well.

$$d_iS = 0 \quad \textit{(reversible processes)} \qquad (2)$$

$$d_iS > 0 \quad \textit{(irreversible processes)} \qquad (3)$$

III. Thermodynamic Fundamentals

In this section and, in order to make easier the afterward discussion, it will be presented the basic classical thermodynamic equations of the problem posed in ref. 1.

The system is one mol of a monoatomic ideal gas at 300 K and 4 bar enclosed in a cylinder with a frictionless piston and whose bottom is in thermal contact with a reservoir at 400 K. The gas is allowed to expand isothermically through an irreversible process up to 1 bar by absorbing a heat Q from the reservoir at T_r.

The entropy change, ΔS_g, of n moles of the gas and, of the reservoir, ΔS_r, are respectively:

$$\Delta S_g = nR\ln\left(\frac{P_i}{P_f}\right) \quad , \qquad (4)$$

$$\Delta S_r = -\frac{Q}{T_r} \quad , \qquad (5)$$

where P_i and P_f are the gas initial and final pressures and, R is the universal gas constant. Since the process is isothermal, then according to the first law $Q = W$, where W is the work done by the gas in the expansion. This quantity can be calculated by appealing that the entropy of the universe, ΔS_u, is the sum of the gas and of the environment. Thus,

$$\begin{aligned} W_{irr} &= nRT_r\ln\left(\frac{P_i}{P_f}\right) - T_r\Delta S_u \ , \\ &= 4610.26J - T_r\Delta S_u \ . \end{aligned} \qquad (6)$$

Up to know, we cannot infer about the value of the irreversible work, W_{irr}, done by the system, since the knowledge of ΔS_u requires to know the amount of the heat, Q, transferred in the process. However, for any transferred Q, ΔS_u can be determined by appealing Prigogine's statement of the Second Law[7]. Accordingly, the total entropy change of a given system, ΔS , is the sum of the internal entropy production, ΔS_i, due to irreversible processes occurring in the system, and the entropy interchange with the environment, ΔS_e. Thus, for the gas we have:

$$\Delta S = \Delta_i S + \Delta_e S \quad , \qquad (7)$$

where $\Delta_e S$ and ΔS_g are defined by:

$$\Delta_e S = \int \frac{dQ}{T} \quad , \tag{8}$$

$$\Delta S_g = \int \frac{dQ_{rev}}{T} \quad , \tag{9}$$

where dQ_{rev} is the heat transferred through an ideal reversible process between the same initial and final states.

Quoting Prigogine: *The entropy increase, $\Delta_i S$ due to changes inside the system, is never negative. It is zero when the system undergoes reversible changes only, but it is positive if the system is subjected to irreversible processes as well."* [7]

With this prescription the entropy production in the gas becomes:

$$\Delta_i S = \int \frac{dQ_{rev}}{T} - \int \frac{dQ}{T} \quad . \tag{10}$$

This is nothing else but the Clausius inequality. For isothermal processes, this is equivalent to $Q_{rev} \geq Q$ and hence $W_{rev} \geq W$. Prigogine statement of $\Delta_i S \geq 0$ is guaranteed by the second law.

From the perspective of the universe, there are two entropy productions: the heat flow from the reservoir and the subsequent irreversible mechanical expansion of the gas. It would be instructive to find these two contributions to the entropy of the universe. The entropy production in the gas is according to Eq. (7), given by:

$$\Delta_i S = \Delta S - \Delta_e S \quad , \tag{11}$$

$$= nR \ln\left(\frac{P_i}{P_f}\right) - \frac{Q}{T} \quad , \tag{12}$$

while the entropy transfer from the surrounding to the vessel , $\Delta_{ht} S$, reads[7]:

$$\Delta_{ht} S = Q\left[\frac{1}{T} - \frac{1}{T_r}\right] \quad . \tag{13}$$

Therefore, ΔS_u is obtained by adding these two equations to give:

$$\Delta S_u = nR \ln\left(\frac{P_i}{P_f}\right) - \frac{Q}{T_r} \quad , \tag{14}$$

which is always positive and furthermore, is in total agreement with Eq. (6) after substituting W by Q because the process is isothermal.

As a matter of comparison, let us rewrite Eq. (6) in terms of Eqs. (13) and (14). It reads as:

$$\begin{aligned} W_{irr} &= nRT_r \ln\left(\frac{P_i}{P_f}\right) - T_r\left(\Delta_i S + \Delta_{ht} S\right) \quad , \\ &= 4610.26 J - T_r\left(\Delta_i S + \Delta_{ht} S\right) \quad . \end{aligned} \tag{15}$$

This is the Eq. (10), or conversely the Eq. (20) of ref. 1.

IV. Problem analysis

This section analyzes the correct interpretation of the equations described in ref. 1. It is important to emphasize that the equations of ref. 1 coincide with those of this manuscript.

It was quoted in page 449 about Eq. (12), corresponding to Eq. (15) in this manuscript:

"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 thermodynamic 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. " [1]

First, there is an inconsistence in acknowledging that $\Delta S_u > 0$ for irreversible processes and that W_{irr} *"should be equal to or less than 4610.26 J"* [1]. That is, having declared that a possible magnitude of the irreversible work should be equal to the threshold value of 4610.26 J, then it has been implicitly assumed that $\Delta S_u = 0$. In thermodynamic language and besides the contradiction incurred, this assertion simply means that a thermodynamic condition reserved only for reversible processes, i.e. $\Delta S_u = 0$, it has been wrongly applied to an equation derived for irreversible ones. This erroneous mechanical interpretation of Eq. (10) in ref. 1, is the key point that leads to predict the violation of the second law, that is, Clausius inequality is wrongly being applied, since it has being assumed that $\Delta S_u = 0$ holds even for irreversible processes. Second, as Eq. (6) states and since $\Delta S_u > 0$, the contribution of the term $T_r \Delta S_u$ will always decrease W_{irr} to values below the maximum work attained between the same initial and final states; otherwise, the second law is overridden since the inequality $W_{rev} > W_{irr}$ could not be satisfied. It is a simple exercise to find the maximum and minimum values for ΔS_u. According to Eq. (6), the maximum can be accomplished by doing an isothermal free expansion for which $W_{irr} = 0$. This gives an upper bound of W_{irr} of 11.525 J/K. Likewise, the minimum would be calculated by executing the irreversible process, in such a way, that W_{irr} were the maximum irreversible work attained in that process. Since the maximum work done by the system can be accomplished only in a reversible way, then for the same initial and final states $W_{rev} > W_{irr}$. Thus, by using Eq. (6) and the standard equation $W_{rev} = nRT\ln(P_i/P_f)$, we find that $\Delta S_u > nR[1-T/T_r]\ln(P_i/P_f)$ which gives $\Delta S_u > 2.881\,J/K$. Therefore, the entropy change of the universe (in units of J/K) for the problem posed in reference 1, lie in the interval (2.881, 11.525), since outside it, any result drawn from Eq. (6) will contradict the thermodynamic second principle. By claiming in page 449 that,

"Therefore, here, we have detected the existence of a set of non conventional isothermal irreversible trajectories, allowed by thermodynamic laws, which produce more work than a reversible transition, between the same initial and final states. This is an unexpected performance not predicted by classical thermodynamics." [1]

it has been implicitly assumed a value of ΔS_u outside this range.

In the discussion of Eq. (20), page 450, of ref. 1, equivalent to Eq. (15) of this manuscript, it was stated:

"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, positive entropy production decreases the ability of the system to do mechanical work, but a negative entropy production enhances the capacity to do work." [1]

Here, we find the same mistake as the one incurred into the analysis of Eq. (10) of [1]. The argument that the positive entropy production due to the heat transfer from the reservoir

"ΔS_{im}, compensates the simultaneous negative entropy production of the ideal gas expansion ΔS_{ig}," [1],

in order to produce more work than in a reversible way is wrong. There is a disagreement with the reading of Eq. (16) of ref. 1 (Eq. (12) in this manuscript), since for any allowed amount of heat transfer Q, the process undergoing into the gas will always produce entropy because of its irreversible nature. By assuming that any of the irreversible processes under consideration, be it the heat transfer or the gas expansion, produce a negative internal entropy production, then Prigogine's global formulation of the second law is contradicted. It clearly states[7]: *"absorption of entropy in one part, compensated by a sufficient production in another part of the system is prohibited. This formulation implies that in every macroscopic region of the system the entropy production due to irreversible processes is positive. The term macroscopic region refers to any region containing a number of molecules sufficiently large for microscopic fluctuations to be negligible".* Thus, from the perspective of the system, all irreversible process, no matter what kind are, are always accompanied by a production of entropy.

Finally, it is important to point out that because of the own characteristics of the whole system, it is impossible to transfer a given Q reversibly, unless the surroundings are adapted to carry out such a process. In this context, the proposal cannot invoke the reversible work of 3457.70 J to be compared with the W_{irr}, since doing that, is missing the fact that the experimental set up have to be adequately fitted to measure those amount of works. By assuming that a temperature gradient of 100 K between the system and its environment produces the work given by Eq. (6) and that, if the transfer would be carried out reversibly to generate 3457.70 J of work, then it has been leaved out that the temperature of the surrounding has to be only infinitesimal larger that of the system. In other words, to achieve the same final state by either a reversible or an irreversible process, it is necessarily to make two different experiments and surprisingly find out that the thermodynamic equations, in particular those referred to the universe, lead to different conclusions in total agreement with the second law. The proposal lacks of this subtlety. It can be detected by reviewing the procedure employed in the derivation of Eqs. (11) and (12) of ref. 1. Thus, immediately after Eq. (10) (Eq. (6) of this note), the proposal states:

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

Afterwards, it correctly appeals that the temperature of the surrounding has to differ infinitesimally from of the system in order to induce a reversible heat transfer. However, it incorrectly derives the expression for the reversible mechanical work, i.e., $W = nRT\ln(P_i/P_f)$ by taking the limit of $T_r \to T$ to Eq. (10) of ref. 1. At first sight the limit process seems obvious because the result matches the desired expression, but a carefully exam of the derivation shows fundamental thermodynamic mistakes which subsequently lead the proposal to claim that the second law can be violated. First, Eq. (10) cannot be used as a starting point to describe a reversible process since it is only valid for irreversible ones. Second, the $T_r\Delta S_u$term involves the entropy change of the universe due to an irreversible process. Therefore, it cannot be related to any reversible change at all, because by making ΔS_u to vanishes, Clausius inequality is wrongly been applied, since its value have to be strictly greater than zero and be lying, as we shown before, into the interval

(2.88,11.52)[J/K]. Third, by matching the two equations by a simple limit procedure, it has been assumed that the two trajectories are infinitesimally apart each other, in spite of, as classical thermodynamic prescribes, the irreversible trajectory is unknown since none of the intermediate states of the irreversible process are truly known. It is important to stress that a reversible or an irreversible process can accomplish the same changes in the gas states, but it is also true that the environment has to be accordingly changed to carry out such a processes. Under these circumstances, the two mechanical works cannot be compared each other to proclaim, as the proposal mistakenly do, the existence of a violating second law process.

It is worth to mention that in a recent paper published in the WWW, di Liberto[9] made a classical and pedagogical extensive analysis of entropy production in irreversible processes, included the one posed in ref. 1 and, correctly proved, as it should be, that entropy production is always positive.

In the next section it will review the main theoretical results on the calculation of the probability of occurrence in macroscopic systems of second law violating molecular processes, i.e., those microscopic processes that destroy entropy instead of producing it.

V. Statistical Mechanics Considerations

Here, it is presented, without any mathematical rigor, the theoretical investigations made on processes that might violate the second law and an important experimental result, which proves that the second principle does not hold at the molecular level.

In 1993, Evans, Cohen and Morris[10] gave an analytical expression, known as the Fluctuation Theorem (FT), for the probability that, for a many-particle system in a non-equilibrium steady state and, for a finite time, the dissipative flows accompanying the irreversible process flows in the reverse direction. As it is well known, any system undergoing a change in its state follows a trajectory in phase space, which is fully described by the Liouville equation. In reversible processes and to guarantee the principle of microscopic reversibility, for each second law-satisfying trajectory, there is by definition an entropy destruction antitrajectory. The FT gives a formula to measure the frequency of those antitrajectories for systems far from equilibrium. It was extended by Evans and Searles[11] to a thermostatted Couette flow and found that the measure of the initial states that subsequently lead to second law violation antitrajectories, those with an accompanying entropy destruction, vanishes exponentially with respect to the time over the occurrence of those violations. They found that the Liapunov exponents, who are the eigenvalues of the stability matrix of the system, are overwhelmingly larger for the antitrajectories so the dynamics follows the more stable producing entropy class trajectories. In 1995, Gallavotti and Cohen[12] gave a proof of the FT for non-equilibrium steady states base on the chaotic hypothesis or Ruelle principle for turbulence [13] and employed, not the Liouvillian measure as Evans et al. did[10], but the generalized Sinai-Ruelle-Bowen measure. Subsequently in 2000, Searles and Evans[14] generalize the transient FT, originally derived in the micro canonical ensemble[10], to other ensembles with different types of thermostats. Additionally, they proof the asymptotic convergence at large times of the transient FT to a more general steady-state FT.

Up to now, all considerations about the scope of the FT mentioned above, have been developed for dissipative systems on which phase space contraction occurs. Thus, Evans, Searles and Mittag[15] check for the validity of the FT for purely Hamiltonian systems (no contraction of the phase space) and found that FT can be applied to conservative systems. However, it would be important to clarify if this prediction works well when it is applied to small sub-regions of a macroscopic system. In this direction, Gallavotti[16] heuristically shown that it might exist a local version of the FT since a local entropy creation rate can be locally defined. Although a systematic procedure to derive the local version has not been developed yet, Ayton, Evans and Searley[17] in 2001, proposed a local FT (LIFT) by integrating the global FT of Evans *et al.*[10] over all transient antitrajectory segments. They contrasted the LIFT with the results of a nonequilibrium molecular dynamic (NEMD) algorithm applied to a Poiseuille flow of a fluid between thermostatted walls and found, that NEMD validates the predictions of their LIFT version.

In conclusion: all theoretical investigations made around the FT predict that for a many-particle system, antitrajectories fade away very shortly with a overwhelming appearance of second law trajectories; that the FT holds where the Prigogine's local formulation of the second law applies and that the probability of observing a second law violation in macroscopic systems is unobservable small.

It is clear that FT has no practical consequences until some experiment can validate it. It came in 2002 when Wang, Sevick, Mittag, Searles and Evans[2] demonstrate and quantitatively confirm the predictions of the FT for transient systems by experimentally following, up to 2 sec after the start, 540 particle trajectories of a collection of 100 6.3 m diameter latex particles captured in an optical trap. For short times of about 0.01 sec the trajectories are distributed nearly symmetrically with a shift towards producing entropy trajectories at longer times, in according to the FT, and with no observation of consuming-entropy trajectories in agreement with the second law. These results were confronted with a molecular dynamics simulation (MDS), giving the same results as the predicted by the FT. The MDS has advantages over the experiment in that many more trajectories can be analyzed. The main conclusion drawn from this experiment is that the appearance of consuming-entropy trajectories over short time scales naturally appear in micron-sized particles with an increasing probability of occurrence when the system get smaller and most importantly, that the behavior of cycling engines running backwards in very small systems violating the second law, are not simple scaled-versions of their macroscopic counterpart.

Another important result, mistakenly used as a theoretical support of the findings in ref. 1, is of Allahverdyan and Nieuwenhuizen[8], in which it is investigated the dynamics of a brownian quantum particle coupled to a quantum thermal bath. It was found that at low temperatures, work could be extracted from the bath in a cycle with a clear violation of the second principle. This perpetuum mobile of a second kind can last for a large, not arbitrarily large, number of cycles. The authors link the violation to the appearance of temporal quantum coherence due to the presence of the slightly off-equilibrium nature of the quantum bath. Of course that this behavior cannot be translated to a macroscopic scale where quantum effects are negligible.

VI. Concluding Remarks

As it was reviewed, there are strong experimental and theoretical evidences that the second law does not hold at the molecular level.

The violations cannot occur at the macroscopic level, such as of reference 1, because of the canceling of statistical fluctuations, as well as, the fast temporal decay of second law violating molecular processes. Most importantly, any conjecture that at the macroscopic world could exist processes contradicting the second principle based on their existence at the microscopic level, is a wrong affirmation due mainly to an incorrect scale transformation.

As J. C. Maxwell remarked in a letter to J. W. Strutt (Lord Rayleigh), dated December, 6th, 1870, about the existence, not proved, of his famous demons[18]: *"The Second Law has the same degree of truth as the statement that "If you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again"."*. In other words, the Second Law holds only on the average at the macroscopic level of description[5].

Finally, as it was well quoted by Freeman in a previous collective discussion[6]: *"The second law of thermodynamics is one of the most highly respected concepts in the pantheon of Science. Despite many attempts to overthrow or subvert it, there has, as yet, been no documented, verifiable, repeatable example of that having been accomplished. That fact does not prove that the second law can never be broken, but it does send the clear message that anyone who proposes a scheme for doing so should expect thorough dissection of the scheme and should be prepared to supply full information about the details of the scheme."*

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