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You certainly know the second law of thermodynamics,
Do you know its connection to other laws of physics and chemistry?

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Abstract

The discovery of the second law of thermodynamics is shortly revisited, with a stress on the unbreakable connection between the second law and the law of energy conservation. The aim is to remind that the second law is an inviolable iron rule. Any presumable violation of this law, even a probabilistic one hinted in the probabilistic interpretation of the second law, inevitably violates the law of energy and mass conservation, and undermines all fundamental laws of physics and chemistry. An alternative approach to interpret the second law, taking into account the multiplicity of paths of random motion in classical mechanics, is discussed.

Keywords: Entropy, second law of thermodynamics, random dynamics, energy, energy conservation, Carnot engine, perpetual motion.

1) Introduction

The second law of thermodynamics (second law for short) stipulates that entropy S always increases in the evolution of an isolated system and remains constant when the system reaches thermodynamic equilibrium. Entropy of a system is defined by its small variation $\delta S = \delta Q/T$ caused by a small quantity of heat δQ absorbed by the system from its surroundings, where T is the absolute temperature of the system evolving in an ideal and extremely slow reversible process [1][2]. For any other process out of equilibrium, also called irreversible process, $\delta S >$

$\delta Q/T$; this is the mathematical expression of the second law. When the system is isolated with $\delta Q = 0$, the second law becomes $\delta S > 0$ as stipulated above¹. According to a widely accepted interpretation, entropy represents a measure of the uncertainty or disorder in the movement of the molecules composing the systems. This idea is reflected in Boltzmann's famous formula $S = \ln W$ where W is the total number of microstates (arrangements of the position and momentum of the molecules) in the system. Larger is W , more the molecules are moving in disorder. The second law means that the system always evolves towards the states having as many as possible microstates, or towards more and more disorder. A good example is the expansion of gas in an isolated recipient from a part of the volume to the empty part, because the number of microstates in the whole volume is larger than in a part of it; the entropy reaches its maximum when the gas uniformly fills the volume in an equilibrium state.

Since its discovery and especially its interpretation given by Boltzmann within statistical mechanics [3][4], the second law has never ceased to raise controversies until today. The most remarkable question is whether the second law is an inviolable fundamental law of nature, as for example Edington very famously insisted² [5], or whether it is just a statistical, or even anthropocentric law subject to possible violation, as proposed by Boltzmann and Maxwell, the two most famous pioneers and protagonists of statistical interpretation [3][4]. The twin demons

¹ It is worth mentioning the entropy is only defined for equilibrium states. It has been extended to non-equilibrium systems changing sufficiently slowly so as to keep local equilibrium and to apply equilibrium thermodynamics using entropy in each of their sufficiently small partitions [6].

² The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations - then so much the worse for Maxwell's equations. If it is found to be contradicted by observation - well, these experimentalists do bungle things sometimes. But if your theory is found to be against the Second Law of Thermodynamics I can give you no hope; there is nothing for it to collapse in deepest humiliation.

of Maxwell³ [7] and of Laplace⁴ [8] remain to date the unvanquished devils haunting the second law, endowed with sharpened facilities, by classical mechanics, to observe and follow the motion of molecules, and to make entropy decrease and even disappear completely [9]. The statistical interpretation of the second law was proposed in this unfavorable context [3][4]; it asserts that the second law (entropy increase) has an overwhelmingly large probability; nevertheless, the probability of entropy decrease is not zero, albeit very small. Obviously, Boltzmann was seeking a reconciliation with the fundamental laws of classical mechanics, to the detriment of the fundamental attribute of the second law.

We often see works claiming observed proofs of violation of the second law [10]. There is even a whole theory under development, based on the fluctuation theorem [11], allowing systematic violation of the second law: for every process in isolated systems where entropy increases by certain amount A with a given probability, there is a nonzero probability of the inverse process yielding the same amount of entropy decrease $-A$. In this frame, the violation of the second law, despite its small probability, becomes a ubiquitous phenomenon in every non-equilibrium thermodynamic process.

The discussions of the validity of second law, since Boltzmann, have been based on the classical mechanics laws, all presumably being valid for the molecules composing thermodynamic systems [3]. As well known, the classical mechanics laws have all been well verified in their own domains for large enough (macroscopic or mesoscopic) systems; its

³ ... if we conceive of a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are as essentially finite as our own, would be able to do what is impossible to us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B , by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B , and only the slower molecules to pass from B to A . He will thus, without expenditure of work, raise the temperature of B and lower that of A , in contradiction to the second law of thermodynamics [7].

⁴ Une intelligence qui, à un instant donné, connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui la composent, si d'ailleurs elle était suffisamment vaste pour soumettre ces données à l'analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'univers et ceux du plus léger atome ; rien ne serait incertain pour elle, et l'avenir, comme le passé, serait présent à ses yeux [8].

extension to microscopic particles may be fraught with difficulties. Quantum mechanics is better qualified for this molecular and atomic scale. However, the optimism of interpreting the second law within quantum mechanics [9] has its limits because many systems obeying second law may be composed of large enough corpuscles obeying classical mechanics. It is of first necessity to address the second law within classical mechanics.

The trouble of the classical mechanics approach to the second law is the conflict between the time *symmetric or reversible* character of mechanics laws and the time *asymmetric or irreversible* character of second law. This is the key point of the debate opposing Boltzmann to Loschmidt⁵. Although this debate remains open today, the Boltzmann's statistical interpretation of second law is one of the widely accepted, probably the surest and simplest way, to make peace between mechanics laws and the second law. The consensus is the following: the mechanics laws are fundamentally inviolable iron rules at any scale; while the second law is only a statistical behavior, sometimes verified, sometimes violated. Put it differently, when an isolated thermodynamic system obeys the second law, it is perfectly normal because it is a consequence of the fundamental laws of mechanics; when the system violates the second law, it is completely normal as well because it is also a consequence of the same fundamental laws. In any case, the classical mechanics laws are fundamental, inviolable, and absolute, no matter what is the behavior of entropy. Moreover, all suggestions of violation give you the impression that the second law is an isolated phenomenon independent of all other physical and chemical phenomena, so that its violation does not have any impact on other laws of physics and chemistry, as if nothing important had happened.

In this paper, we address this debate under a different angle to show that this isolation of the second law is illusory. The second law actually has a vital connection to other fundamental laws, especially to the law of conservation of energy and mass. For this purpose, we propose to revisit succinctly the history of the discovery of the second law. In the course of those exploits from Carnot [1], Kelvin[17] to Clausius [2], we cannot but notice that the second law and the energy law are mutually conditioned, like conjoined twins. Energy conservation is a necessary condition for the second law (no energy conservation, no second law). Inversely, if the second law is broken, the law of energy conservation collapses at once.

⁵ https://en.wikipedia.org/wiki/Loschmidt%27s_paradox

After this demonstration, we discuss a new approach to the reconciliation between mechanics laws and second law. This approach is different from statistical mechanics in that it takes into account a key characteristic of random motion: the multiplicity of paths; this is the fact that a random motion can take different paths from a given initial state, contrary to classical mechanics motion taking only a single unique path from a given state. In this framework, the obstacles to the entropy increase of the second law, such as Liouville's theorem [12], Poincaré's recurrence theorem [13], and time symmetry [15], are removed once and for all [16][21]. Detailed discussion is given in the concluding remarks.

2) Discovery of entropy

We see sometimes in textbooks that the second law is an empirical finding⁶. It is not true. The discovery of the second law is actually a result of pure thought experiments and mathematical calculations.

The history of entropy has something to do with a decree of the Academy of Science of Paris in 1775 deciding not to examine any proposition of perpetual mobile machines⁷ [14]. Since then, the impossibility of perpetual mobile began to be taken for granted on the basis of a common belief that energy and motion cannot be created from nothing [1]; the law of energy conservation was not yet known to the scientific community at that time. Today we have the mathematical proof that this machine cannot exist because it violates the law of conservation of energy. This decree is the starting point of the remarkable work of Carnot in the study of the efficiency of thermal engine [1], leading to the second law many years later. We can at once guess that there must have some vital connection between the second law and its starting hypothesis. In order to highlight this connection and the mathematical rigor in it, we will retrace the impressive trilogy from the impossibility of perpetual mobile all the way to the discovery of the second law. The reader will see a summary of the key elements of the story below. The details of the mathematics are described in **Appendix**.

⁶ https://en.wikipedia.org/wiki/Second_law_of_thermodynamics

⁷ A dream of many engineers of that time is to construct what is called today the perpetual mobile of first kind, a machine that can produce unlimited amount of work without consuming heat or other forms of energy.

a) *From perpetual mobile to Carnot theorem*

Carnot was concerned with heat engine and its efficiency. In 1824, he published the extraordinary idea of a reversible heat engine⁸, now called Carnot engine. This ideal engine can work in a reversible cycle between two reservoirs of heat, one at higher temperature t_1 and the other at lower temperature t_2 . The reversible cycle means that the engine can work in a forward cycle, extract a heat Q_1 from t_1 , reject a heat Q_2 ($<Q_1$) to t_2 and produce a mechanical work $W = Q_1 - Q_2$; it can also backtrack the same cycle inversely, extract the heat Q_2 from t_2 , consume the work W , and reject the heat Q_1 to t_1 . Carnot engine works in both directions with the same efficiency defined by $\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$. The capacity of this reversible engine is extremely nontrivial because such a machine cannot exist. It is impossible for a real machine to perform such reversible operation due to friction or other form of energy loss. So all real engines are irreversible machines. With the help of this his magic machine, Carnot discovered the efficiency limit for all possible engines; he described this discovery in the first part of his theorem, asserting that⁹:

All irreversible heat engines between the two reservoirs are less efficient than the reversible engine working between the same reservoirs.

Carnot proved this theorem by *reductio ad absurdum* based on the impossibility of perpetual mobile¹⁰. The details of his proof are illustrated in **Appendix i**. To summarize, this theorem is true if and only if the perpetual mobile does not exist. In other words, if an irreversible engine working between the same reservoirs is more efficient than the Carnot engine, we can then use this irreversible engine to construct a perpetual mobile engine (**Figure A1 of Appendix i**) to produce energy with no need of energy source; this engine would solve our big worry about renewable energy source and environment¹¹.

We will see below that the meaning of the existence of this perpetual mobile is much deeper than giving a solution to our energy concern. This first part of Carnot theorem is crucial for the

⁸ Ref [1], pp17-20

⁹ Le maximum de puissance motrice résultant de l'emploi de la vapeur est aussi le maximum de puissance motrice réalisable par quelque moyen que ce soit. Ref [1], p22

¹⁰ Ref [1], pp21-22

¹¹ Ref [1], p22

discovery of the second law. But this discovery would be impossible without the second part of Carnot theorem.

The second part of Carnot theorem is somewhat implicit in the first part. Since the Carnot engine is the most efficient of all possible engines, all Carnot engines, each working with a different substance (air, steam, etc.), must be equally efficient. If two Carnot engines were not equally efficient, we would be able to replace the first irreversible engine in the Carnot's proof (**Appendix i**) by this more efficient Carnot engine, in order to make a perpetual mobile. If all Carnot engines have the same efficiency regardless of their working substances, then this efficiency, say, η , can only depend on the temperatures of the reservoirs t_1 and t_2 . The second part of the theorem states:

All Carnot engines have the same efficiency regardless of their working substances; this efficiency only depends on the temperatures of the reservoirs: $\eta(t_1, t_2)$.

For Carnot, the only interest of his magic engine is to specify the limit of the efficiency of all possible heat engines. A practical question is how to calculate this limit $\eta(t_1, t_2)$ when the temperatures of reservoirs are given? Physicists had to wait about thirty year to see the answer given by Kelvin [17].

b) Kelvin's efficiency of Carnot engine

In 1854, Kelvin found the expression of $\eta(t_1, t_2)$ by considering the second part of the Carnot theorem and using a new scale of temperature called absolute temperature denoted by T [17]. The expression is

$$\eta = 1 - \frac{T_2}{T_1} \tag{1}$$

for a Carnot engine working between two reservoirs of absolute temperature T_1 and T_2 ($T_1 > T_2$). This expression can be found in a general way using a combination of two Carnot engines in series, the first one working between the reservoir 1 at T_1 and the reservoir 2 at T_2 ($T_1 > T_2$), the second one working between the reservoir 2 and the reservoir 3 at T_3 ($T_2 > T_3$). The mathematic tricks are straightforward as shown in **Appendix ii**. This expression is an unavoidable consequence following the second part of the Carnot theorem that the efficiency only depends on the temperatures of the two reservoirs.

Now let ΔQ_1 be the heat absorbed by the Carnot engine from reservoir 1, and ΔQ_2 the heat it “absorbs” from reservoir 2 (it actually rejects $-\Delta Q_2$ to reservoir 2). After a cycle, the engine returns to the reservoir 1, and produces a positive work $W = \Delta Q_1 - (-\Delta Q_2)$, we can write $\eta = \frac{W}{\Delta Q_1} = 1 - \frac{(-\Delta Q_2)}{\Delta Q_1} = 1 - \frac{T_2}{T_1}$, leading to $\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0$. Suppose now the number of the reservoirs contacted by the engine during a cycle is N , the i^{th} reservoirs ($i = 1, 2 \dots N$) at temperature T_i gives δQ_i to the engine, Kelvin obtained

$$\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0 \quad (2)$$

Then he stopped here in his quest of the second law without reaching the concept of entropy [17][18].

c) Clausius' perception

The very discovery of what is called the second law finally came to Clausius who, like Kelvin, reached also Eq.(2) [2]. But he saw something deeper in it. If the number of reservoirs contacted by the engine is very large, Eq.(2) takes the form of a closed line integral : $\oint \frac{\delta Q}{T} = 0$. This integral over a reversible cycle implies that the quantity $\frac{\delta Q}{T}$ is the variation of a state variable, he denoted by S , of the engine. During the contact with a reservoir at T , the engine gets δQ as well as a variation of S : $dS = \frac{\delta Q}{T}$. After a cyclic evolution, the engine comes back to its initial state, the total variation of S is zero: $\oint dS = \oint \frac{\delta Q}{T} = 0$.

Clausius didn't stop here with $dS = \frac{\delta Q}{T}$ for reversible process. He had the genius idea to make the same analysis as above for a real irreversible engine, of efficiency η' , cycling between the same reservoir 1 and 2, absorbing ΔQ_1 and ΔQ_2 , and doing a work W' after a cycle. We have $\eta' = \frac{W'}{\Delta Q_1} = 1 - \frac{(-\Delta Q_2)}{\Delta Q_1}$. But this time he considered the first part of Carnot theorem $\eta' < \eta$, and Kelvin's limit $\eta = 1 - \frac{T_2}{T_1}$, to write

$$1 + \frac{\Delta Q_2}{\Delta Q_1} < 1 - \frac{T_2}{T_1} \quad (3)$$

which means $\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} < 0$. For a large number of reservoirs on the cycle, he wrote $\oint \frac{\delta Q}{T} < 0$, which yields (see **Appendix iii**):

$$dS \geq \frac{\delta Q}{T} \quad (4)$$

for both irreversible ($>$) and reversible ($=$) processes. Clausius coined the name *entropy* for this variable S because he wanted to find a Greek word that is parallel and analogous to the Greek word *energy*¹² [19]. He certainly felt some intrinsic link between energy and entropy; himself had just at that time proposed the first law of thermodynamics of energy conservation [20].

3) If we backtrack the trilogy

By summarizing the trilogy of discovery of the second law, we wanted also highlight the impressive and infallible mathematical tricks going from the impossibility of perpetual mobile all the way to the second law. These rather straightforward mathematical deductions show that, if perpetual mobile is impossible, then there must be the Carnot theorem, and then the second law follows; you cannot get other thing different; and inversely, if the second law is broken, i.e., Eq.(4) breaks down, you can backtrack all the mathematical calculations of Clausius from Eq.(2) to Eq.(4), to prove Eq.(3) untrue. Eq.(3) stems from Eq.(1) and the first part of Carnot theorem. Its falseness implies either the falseness of Eq.(1) or that of the first part of Carnot theorem.

Now suppose Eq.(1) is false, in view of the infallible mathematics of Kelvin using **Figure A2 (Appendix ii)**, the second part of Carnot theorem must be untrue. In other words, different Carnot engines using different working substances may have different efficiencies. According to the discussion in the section 3a), we will be able to construct a perpetual mobile using two Carnot engines of different efficiencies.

If now we suppose Eq.(1) and the second part of the Carnot theorem are true but the first part of the theorem is false, so there may be engines more efficient than Carnot engine. Then we can use these more efficient engines, as shown in **Figure A1 of Appendix i**, to fabricate perpetual mobiles, which will give us infinite quantity of clean energy we need to preserve our pet planet.

¹² I prefer going to the ancient languages for the names of important scientific quantities, so that they may mean the same thing in all living tongues. I propose, accordingly, to call the entropy of a body, after the Greek word 'transformation.' I have designedly coined the word entropy to be similar to 'energy,' for these two quantities are so analogous in their physical significance, that an analogy of denomination seemed to me helpful [19].

To summarize, the violation of the second law necessarily entails the existence of perpetual engine. Well, perpetual engine and free source of energy come into being! Granted! So what!

4) So what if the second law is violated?

The most important implication of the violation of second law is not the existence of perpetual mobile as a source of infinite energy. There is another much deeper meaning behind the perpetual mobile : energy becomes something you can create or annihilate as much as you please, and loses at once the attribute of a conservative fundamental quantity of motion, regardless of its form, thermal, mechanical, electromagnetic, gravitational, and so on. The first mathematical consequence is the collapse of the first law of thermodynamics $dU = \delta Q + dW$. Why? Because after a cycle of the perpetual engine in the **Figure A1** of **appendix i** for instance, $dU = \delta Q = 0$, but $dW \neq 0$; this is the work done by the perpetual engine without consuming heat. Needless to say, the whole theoretical edifice of the thermodynamics will collapse.

This is not all. As well known, energy conservation is not only one of the cornerstone of thermodynamics, it is also a key pillar of the whole edifice of physical and chemical science, as well as a fundamental rule guaranteeing the stability of all natural systems. For example, our pet planet is in stable revolution around the sun because its total mechanical energy remains constant (conserved) when the pair earth-sun is a good isolated system, at least for a period sufficiently long for our intelligence to develop, fortunately. Now if the energy of the isolated earth-sun was no longer a constant due to a perpetual engine in the system modifying arbitrarily the energy of the earth without changing anything else, the earth would have fallen in the sun or flight to the border of Milky Way since long. Please make the same reasoning for nuclei, atoms, molecules and any energy conservative system in Nature; do you think that they can be there as stable components our universe? Imagine also that you want to make a solid state synthesis; you put the prepared sample in the oven and increase the temperature to 1000 K. But one day you realize that the sample is freezing! Why? Because the heat is flowing from the colder sample into the hotter oven, a direct consequence of the violation of the second law and of the energy conservation! Think also that most, if not all, fundamental equations in physics and chemistry are based on the energy and mass conservation. Energy and mass are connected

by Einstein's equivalence formula¹³; so if energy is not conserved, the mass neither. We would see the disappearance of Newtonian equation, Maxwell equations, chemical reaction equations, stoichiometry formula, Maxwell's equations, Fick's laws of diffusion, Einstein's equation of general relativity, and, finally, Schrödinger equation! After these losses, what does remain in physics and chemistry?

Indeed, when the violation of the second law is regarded as isolated phenomenon, it looks like something plausible and interesting even exciting to talk about. However, when it is coupled to the violation of the law of energy conservation, we quickly understand to what extent the second law of thermodynamics is an inviolable iron rule. Can we imagine a violation of energy and mass conservation, even probabilistic with infinitesimal likelihood, as the fluctuation theorem stated for second law violation [10][11]? Can we imagine that energy and mass are no more conservative quantities? Simply we cannot! That would be a fatal menace for the whole edifice of physics and chemistry, and the whole nature as well, since it would risk collapsing into nil even if the violation of the second law and of energy-mass conservation took place during only a fraction of second. Now we understand better the comment of Edington about the violation of the second law (footnote p.2) [5].

5) Concluding remarks

We have shown that the second law of thermodynamics is not an isolated phenomenon on its own in nature. There is an unbreakable connection between this law and the law of energy-mass conservation as well as other fundamental laws of physics and chemistry. The violation of the second law would lead to fatal failure of energy and mass conservation, implying the collapse of the whole physics and chemistry science. Any claim of violation is necessarily questionable. We would say that if a theory goes into conflict with the second law, the only possible explanation is either the theory is fallacious or the "entropy" violated is not the entropy of the second law.

The suggested violation of the second law is tightly related to a remarkable discordance in statistical mechanics between two concepts. The first is entropy as a measure of the dynamic uncertainty in the motion of the particles in thermodynamic systems; the second is the motion

¹³ In relativity theory, we have $E = mc^2$, where E is energy, m the mass, and c the velocity of light in vacuum; see https://en.wikipedia.org/wiki/Mass%E2%80%93energy_equivalence

of these molecules presumably obeying the laws of Newtonian mechanics. There is a discordance because motion within Newtonian mechanics does not contain any uncertainty, being deterministic and perfectly predictable either to the past or to the future [21]. The twins of Maxwell's and Laplace's demons mentioned above [7]-[9] are just a product of this absence of dynamic uncertainty. Any supposed uncertainty measure in this framework not only carries a subjective character, but also is subject to several constraints, such as Liouville's theorem [12], the eternal return of Poincare's theorem of recurrence [13] and time symmetry dictated by the fundamental principle of least action [21]. On the one hand, Liouville's theorem states that the density of states ρ in the phase space of a systems is a constant of motion, i.e., $\frac{d\rho}{dt} = 0$. If the motion becomes random, the probability distribution of states of the system is proportional to ρ . So that any function of ρ , like the Boltzmann H -function $H(\rho)$ and entropy $S(\rho)$ [3], must be also constant in time because $\frac{dH(\rho)}{dt} = H'(\rho) \frac{d\rho}{dt} = 0$. This is at odds with the second law of increasing entropy. On the other hand, Poincare's theorem of recurrence states that, during its movement in phase space, a real system always returns arbitrarily close to its initial states, implying that any function of states, including entropy, cannot only increase. If it increases during some periods, it must decrease in other periods in order to recover its initial value when the system returns to its initial states. This is again at variance with the second law stating that entropy never decreases.

As these theorems are irrefutable in Newtonian mechanics, a possible, if not the only, pathway to escape from these constraints is the probabilistic interpretation of the second law stating that, although entropy can both increase and decrease, the second law is always observed because the entropy has an overwhelmingly larger probability to increase than to decrease [3]. This implies that the decrease of entropy, or the violation of the second law, has nevertheless an infinitesimal probability to occur. Indeed, at first glance, a possible violation of the second law, not that often, seems acceptable to the detriment, at worst, of the Carnot engine as a king of all engines. However, when considering the unbreakable connection between the second law and other fundamental laws of physics, especially the parallel violation of the law of conservation of energy, we should be more vigilant.

It is obviously that this deadlock of probabilistic interpretation of the second law is a telltale sign of the incompatibility between classical mechanics laws and thermodynamics laws. This is indeed a nontrivial conflict between two families of physics laws, both being inviolable truth and well verified by empirical facts. We have to find a reconciliation between them in order to

keep them all in a big family. A possible solution can be perceived in the difference between the classical mechanics motion and the thermodynamic motion. All motions in classical mechanics are regular and deterministic, characterized by the unicity of path for given initial condition, or between any two states, a single path dictated by the least action principle [12]. This motion is predictable to both the past and the future with certainty on the unique path predetermined by the equation of motion (Newtonian or relativistic). On the contrary, the thermodynamic motions are all random, or indeterministic, characterized by multiplicity of paths from given initial state. That is, leaving a given state, a motion can take different paths. In other words, there are infinite paths between any two given states. The motion becomes completely unpredictable or only predictable with more or less uncertainty depending on the probability of the all the possible paths. In this regime, the fundamental principle of least action and the equations of motion, working only for unique path must be adapted in such a way to include many paths and their probability. The new formalism must also allow recovering the original principles and equations of motion of classical mechanics whenever the randomness cancels and the multiple paths all collapse onto a single path of probability one.

A formulation of this kind has been proposed in previous works [22]-[25] for the special case of random motion of quasi-Hamiltonian systems, i.e., mechanical systems undergoing random motion but statistically conserving their energy. A good example of this kind of Hamiltonian systems is the ideal gas. When a gas is in expansion, it moves randomly from one equilibrium state to another, in keeping its energy constant within fluctuations, and following different paths, each having a given probability to happen between the initial and final states. This path probability has been investigated by analytical analysis [26] and numerical experiments simulating random motions with different randomness [27][28]. The reader can find a summary of this probabilistic mechanics in [25]. We would like to just mention that, in this frame, Liouville's theorem, originally formulated for the unique path of least action [12], has been modified for multiple paths and reads $\frac{d\rho(t)}{dt} = \rho(t) w(t)$, where $w(t)$ is proportional to the work of random forces around a given point in the system. The solution of this differential equation is $\rho(t) = \rho_0 \exp[-\int_0^t w(t) dt]$. This modified Liouville's theorem invalidates the proof of Poincare's theorem of recurrence, thus opens the way for a non-probabilistic interpretation of the H-theorem and the second law of thermodynamics [16][25]. Whenever the random force is absent, or the system does not evolve any longer in an equilibrium state, the work $w(t) = 0$, Liouville's theorem $\frac{d\rho(t)}{dt} = 0$ is recovered.

We would like to close this paper by mentioning a recent work, in which we provided a mathematical proof of time irreversibility within classical mechanics in a very general and model-independent way, by considering the multiplicity of paths of random motion [21]. For the first time, the concept of time was shown to have an arrow pointing in the direction of increasing dynamic uncertainty, just as Edington asserted a hundred years ago: *Without any mystic appeal to consciousness it is possible to find a direction of time ... Let us draw an arrow arbitrarily. If as we follow the arrow we find more and more of the random element in the state of the world, then the arrow is pointed towards the future; if the random element decreases, the arrow points towards the past. That is the only distinction known to physics. This follows at once if our fundamental contention is admitted that the introduction of randomness is the only thing which cannot be undone* (see [5] p.35).

The same statement is true for the arrow of entropy as well.

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Appendix

This is a summary of the trilogy of the discovery of the second law of thermodynamics over thirty years starting from 1824.

i) Carnot theorem from a thought experiment

Figure A1 illustrates a combination of an irreversible real engine and a reversible Carnot engine, both working between a hot reservoirs at temperature t_1 and a cold reservoir at temperature t_2 . The irreversible engine produces a work $W' = Q_1 - Q_2$ in absorbing a heat Q_1 from the hot reservoir and rejecting a heat Q_2 to the cold reservoir. Its efficiency is given by $\eta' = \frac{W'}{Q_1}$. The reversible engine is working in the inverse direction using a work W to absorb the heat Q_2 from the cold reservoir and give a heat Q_1 to the hot reservoir. Its efficiency is given by $\eta = \frac{W}{Q_1}$. After a cycle, the two reservoirs recover their initial states respectively because they didn't obtain nor lose heat.

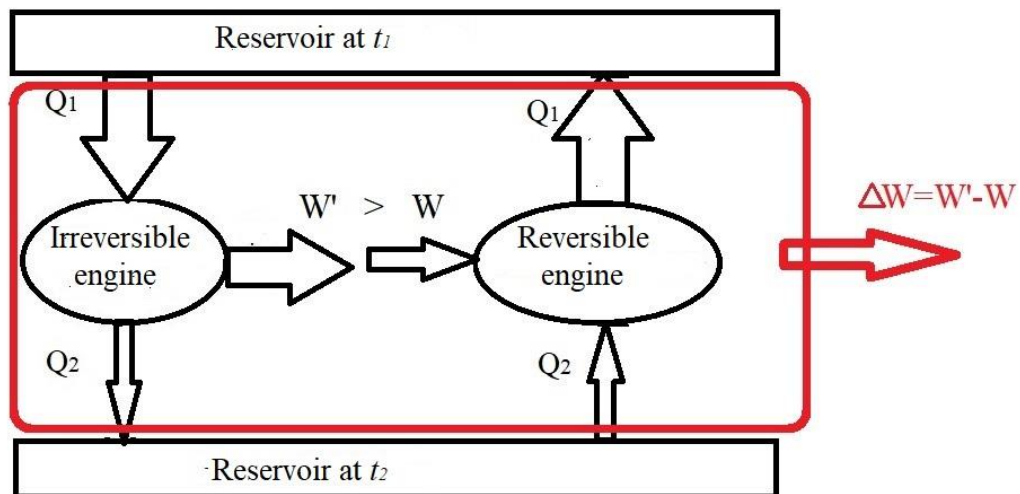


Figure A1, Illustration of a perpetual mobile engine (red line) composed of a real irreversible engine having efficiency $\eta' = \frac{W'}{Q_1}$ and a Carnot engine having the efficiency $\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$. If $\eta' > \eta$, the perpetual engine is able to produce the work $\Delta W = W' - W$ after each cycle without consuming heat, so that the energy ΔW is created from nothing.

Now Carnot supposed that the irreversible engine has a larger efficiency than the reversible engine, $\eta' > \eta$, or $\frac{W'}{Q_1} > \frac{W}{Q_1}$, leading to $W' > W$. In this case, the reversible engine can use a part of W' to produce the work W , so that after a cycle, the only thing changed is the extra work $\Delta W = W' - W > 0$ produced by the ensemble of two engines (red line in **Figure A1**). This means that the ensemble of two engines is a perpetual engine producing the work ΔW from nothing, which Carnot thought impossible according to a common belief that mechanical work and motion cannot be created from nothing (a rudimental idea of energy conservation). Conclusion: η' can never be larger than η ; which is the first part of Carnot theorem $\eta' \leq \eta$ [1].

From the same reasoning, we can prove that all reversible engines must have the same efficiency regardless of their different working substances. This is because if a reversible engine was more efficient than another one, we could combine them in the same way as in **Figure A1** with the more efficient Carnot engine replacing the irreversible one; this would make a perpetual engine (absurd). Conclusion: *all Carnot engines must have the same efficiency depending only on the temperatures of the reservoirs t_1 and t_2* , which is the second part of Carnot theorem [1].

ii) Kelvin's efficiency

It is quite logical that the efficiency η of Carnot engine depends only on the temperature of the reservoirs. But what is the form of the function $\eta(t_1, t_2)$? Kelvin is concerned with this question, and made a calculation [17] which can be illustrated by the connection of two Carnot engines as shown in **Figure A2**. The first engine works between two reservoirs at t_1 and t_2 ($t_1 > t_2$), absorbing Q_1 from t_1 , rejecting Q_2 to t_2 and doing a work $W_1 = Q_1 - Q_2$; the efficiency is $\eta_1 = 1 - \frac{Q_2}{Q_1}$. The second engine works between the above reservoir at t_2 and a third reservoir at t_3 ($t_2 > t_3$), absorbing Q_2 from t_2 , rejecting Q_3 to t_3 , and doing a work $W_2 = Q_2 - Q_3$; its efficiency is $\eta_2 = 1 - \frac{Q_3}{Q_2}$. On the other hand, these two engines connected in series can be considered as a third engine, working between the hot reservoir at t_1 and the cold reservoir at t_3 ($t_1 > t_3$), absorbing Q_1 from t_1 , rejecting Q_3 to t_3 , and doing a work $W_3 = W_1 + W_2 = Q_1 - Q_3$; its efficiency is $\eta_3 = \frac{W_3}{Q_1} = 1 - \frac{Q_3}{Q_1}$.

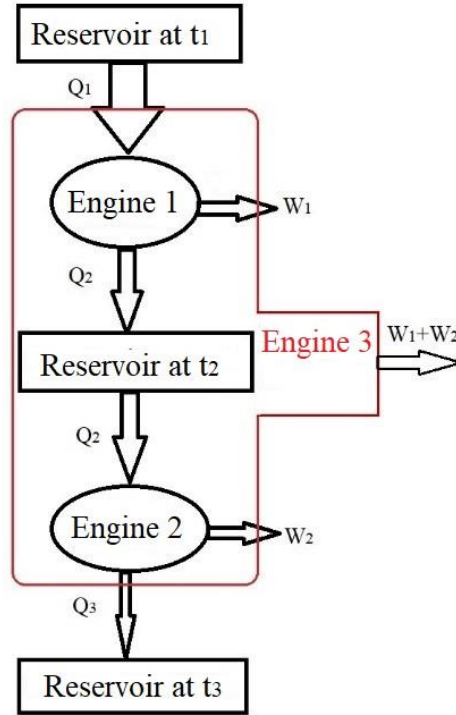


Figure A2: Illustration of Kelvin's idea to connect two Carnot engines in series to compose a third Carnot engine (red line) working between t_1 and t_3 .

The magic trick is the following: from the three efficiencies $1 - \eta_1 = \frac{Q_2}{Q_1}$, $1 - \eta_2 = \frac{Q_3}{Q_2}$ and $1 - \eta_3 = \frac{Q_3}{Q_1}$, it is straightforward to write $(1 - \eta_1)(1 - \eta_2) = 1 - \eta_3$. As all Carnot engines have the same efficiency depending only on the temperature of the reservoirs, we can write $1 - \eta_1 = g(t_1, t_2)$, $1 - \eta_2 = g(t_2, t_3)$ and $1 - \eta_3 = g(t_1, t_3)$, leading to $g(t_1, t_2)g(t_2, t_3) = g(t_1, t_3)$, where $g(\cdot)$ is any continuous function. The only way to reach this last equation is to let $g(t_1, t_2) = \frac{f(t_2)}{f(t_1)}$, $g(t_2, t_3) = \frac{f(t_3)}{f(t_2)}$ and $g(t_1, t_3) = \frac{f(t_3)}{f(t_1)}$ with certain function $f(t)$. Now let us simply take $f(t)$ as a temperature scale, say, $f(t) = T$, which turns out to be the absolute temperature. Kelvin finally got $1 - \eta_1 = \frac{T_2}{T_1}$, $1 - \eta_2 = \frac{T_3}{T_2}$ et $1 - \eta_3 = \frac{T_3}{T_1}$, or in general, for a Carnot engine working between T_1 and T_2 ($T_1 > T_2$): $\eta = 1 - \frac{T_2}{T_1}$ [17].

iii) Clausius' discovery

Clausius' work [2] starts with a Carnot engine working between T_1 and T_2 . He writes $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$, or $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$, and $0 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$. With a change of notation $\delta Q_1 = Q_1$, and $\delta Q_2 = -Q_2$, he obtained $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$. Notice that δQ is a heat absorbed by the engine from a reservoir (see **Figure A3**). Obviously, if the engine is in contact with N reservoirs during a cycle, and absorbs δQ_i from a reservoir at T_i , we necessarily get $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0$ (**Figure A3**).

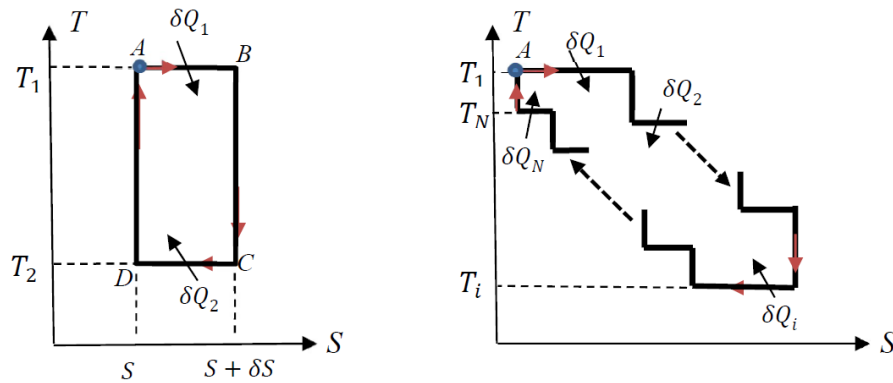


Figure A3: Examples of the cycle of Carnot engine in the $T - S$ diagram. The horizontal segments represent the contact of the engine with the reservoirs to absorb heat. The vertical segments represent adiabatic compression (left sides) and expansion (right sides). **Left** : a cycle starting from and ending at an initial state A after two contacts with T_1 and T_2 , leading to $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$. **Right** : a cycle starting from and ending at the initial state A after the contacts with N reservoirs at different temperature T_i , each giving δQ_i to the engine, leading to $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = 0$.

Clausius understood at once that $\frac{\delta Q}{T}$ is the variation of a variable of state, he denoted by S ($\delta S = \frac{\delta Q}{T}$) and coined the name *entropy*, because when the engine comes back to its initial state after a cycle and a series of variations $\frac{\delta Q_i}{T_i}$, this variable also comes back to its initial value with zero variation $\sum_{i=1}^N \frac{\delta Q_i}{T_i} = \sum_{i=1}^N \delta S_i = 0$. If N is vary large, we can write a closed line integral $\oint dS = 0$ over a cycle.

Clausius made the above analysis with Carnot engine. What does happen with a real irreversible engine working between the same reservoirs with $\eta' = 1 - \frac{Q_2}{Q_1}$? Considering $\eta' < \eta$ and $\eta = 1 - \frac{T_2}{T_1}$, we get $1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$ or $\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0$. The same formal change as above yields $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} < 0$. With N reservoirs during a cycle, we have $\sum_{i=1}^N \frac{\delta Q_i}{T_i} < 0$ or $\oint \frac{\delta Q}{T} < 0$. Suppose that the variation of entropy of the engine at each equilibrium contact with a reservoir is δS_i , we have, after a cycle, $\sum_{i=1}^N \delta S_i = 0$, or $\oint dS = 0$ for large N . Compare $\oint dS = 0$ to $\oint \frac{\delta Q}{T} < 0$, it is straightforward to write $dS > \frac{\delta Q}{T}$ for irreversible engine, or $dS \geq \frac{\delta Q}{T}$ for any engine, reversible or irreversible. This inequality is the mathematical expression of the second law of thermodynamics. For an isolated system without exchange of heat with the exterior, $\delta Q = 0$, and $dS \geq 0$. This is why the second law is often referred to as the law of increasing entropy. Notice that the entropy of an open system exchanging heat with environment has $dS \geq \frac{\delta Q}{T}$ and can decrease ($dS < 0$) if the system loses heat $\delta Q < 0$ (like our body); this decrease does not violate the second law. Again, *the violation of the second law implies the decreases of entropy in an isolated system.*