The peculiar status of the second law of thermodynamics and the quest for its violation

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ABSTRACT

Even though the second law of thermodynamics holds the supreme position among the laws of nature, as stated by many distinguished scientists, notably Eddington and Einstein, its position appears to be also quite peculiar. Given the atomic nature of matter, whose behavior is well described by statistical physics, the second law could not hold unconditionally, but only statistically. It is not an absolute law. As a result of this, in the present paper we try to argue that we have not yet any truly cogent argument (known fundamental physical laws) to exclude its possible macroscopic violation. Even Landauer's information-theoretic principle seems to fall short of the initial expectations of being the fundamental 'physical' reason of all Maxwell's demons failure. Here we propose a modified Szilard engine which operates without any steps in the process resembling the creation or destruction of information. We argue that the information-based exorcisms must be wrong, or at the very least superfluous, and that the real physical reason why such engines cannot work lies in the ubiquity of thermal fluctuations (and friction).

We see in the above peculiar features the main motivation and rationale for pursuing exploratory research to challenge the second law, which is still ongoing and probably richer than ever. A quite thorough (and critical) description of some of these challenges is also given.

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1. Introduction

In its classical and phenomenological formulation, the second law of thermodynamics states that "it is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of the heat from a cooler to a warmer body" (Clausius formulation) or, equivalently, that "it is impossible to construct a device that, operating in a cycle, will produce no effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work" (Kelvin–Planck formulation).

Then, the thermodynamic state-function entropy S was discovered. It is defined up to an additive constant as the following integral through a quasi-static reversible path (Fig. 1),

$$\Delta S = S_B - S_A = \int_A^B \frac{\delta Q}{T}, \qquad (1)$$

where A and B are two points in space-state of a thermodynamic system, T is the absolute temperature of the system, δQ is the inexact differential of the heat Q (the heat gained by the system).

The second law can be stated in the well-known *increasing entropy* formulation: whenever an adiabatically isolated system evolves from equilibrium state A to equilibrium state B, the variation of entropy ΔS cannot be negative, $\Delta S \geq 0$ (Fermi, 1956).

2. The status of the second law

Even though the second law "holds the supreme position among the laws of Nature" (Eddington, 1929), its position appears to be also quite peculiar. When the theory of statistical physics was developed by Maxwell, Boltzmann and others, it became clear very quickly that the second law of thermodynamics could not hold unconditionally, but only statistically. The Brownian motion is a well-known macroscopic example of that, as early noted by Poincarè. In other words, entropy of isolated systems is not forbidden to decrease, but in all processes the *probability of*
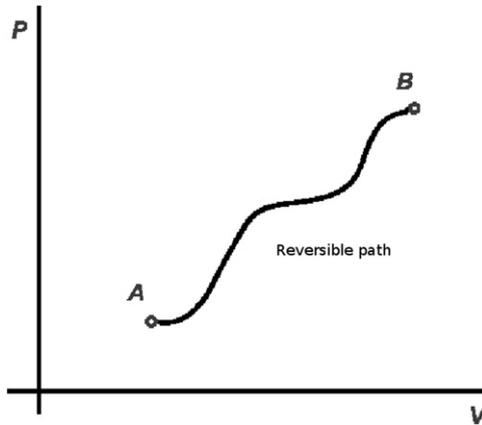
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Fig. 1. Transformation of a thermodynamic system from state A to state B through a reversible path in the volume–pressure (V,P) diagram. The third thermodynamic variable, temperature T, depends on V and P through the equation of state of the system.
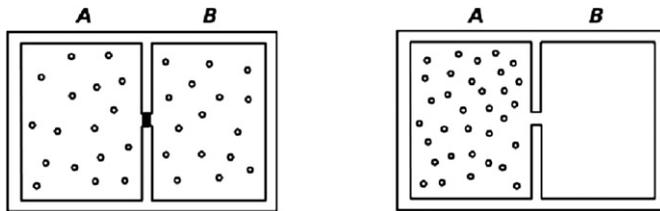

Fig. 2. The gas-in-two-chambers thought experiment described in the text.

continuous and macroscopically significant (and also able to provide usable work) entropy decrease is extremely small.

Consider, for instance, a container separated into two sections, A and B, by a diaphragm. Both chambers contain the same amount of ideal gas, e.g. 10^{23} particles each,[1] and are at the same temperature T (Fig. 2). If the partition which separates chamber A from chamber B is removed, then nothing prevents particles in chamber A from freely moving to chamber B, and vice-versa. Assuming the interaction between particles negligible (we are dealing with an ideal gas), the behavior of each particle should be uncorrelated with respect to every other particle and there is a non-zero chance that, at some moment, all the particles of both chambers are confined in chamber A. If one observes the system, the probability of finding a specific particle in chamber A is obviously equal to $\frac{1}{2}$, thus the probability that, at some moment, all the particles are in chamber A is

$$P_{A\&B \to A} = \left(\frac{1}{2}\right)^{2\times 10^{23}} \simeq 10^{-6\times 10^{22}}. \tag{2}$$

The above probability is an incredibly tiny one, but it *is not* zero. If the total length l of the two-chamber container is 1 m and the mean velocity $\langle v \rangle$ of the particles is $\sqrt{8kT/\pi m}$, where k is Boltzmann's constant, T the absolute temperature of the gas and m is the mass of one particle ($\langle v \rangle$ can be derived from the Maxwell–Boltzmann velocity distribution), then the order of magnitude of the average time τ one particle takes to go from

chamber A to chamber B, or vice-versa, is given by

$$\tau = \frac{l}{\langle v \rangle} = \sqrt{\frac{\pi l^2 m}{8kT}} \simeq 5.6 \times 10^{-4} \text{ s}, \tag{3}$$

where for m we chose the mass of the lightest gas molecule (hydrogen molecule) and for T the room temperature 298 K.

One can see τ as the *clock-time* at which the system of particles changes its configuration. Hence, the mean time $\langle T \rangle$ one has to wait to observe an exceptional occurrence like that described above (all particles in chamber A) is nearly,

$$\langle T \rangle = \frac{\tau}{P_{A\&B \to A}} \simeq 10^{6\times 10^{22}} \text{ s}. \tag{4}$$

Note that this time is nearly $10^{6\times 10^{22}}$ times the estimated age of the Universe ($\sim 10^{17}$ s) since $10^{6\times 10^{22}}$ s$/10^{17}$ s $\approx 10^{6\times 10^{22}}$.

Thus, no one will ever have the chance to observe such an occurrence, but this does not mean that it is forbidden by the fundamental laws of physics.

For the sake of completeness, let us show why the above situation is a violation of the second law of thermodynamics. Let us calculate the entropy variation $\Delta S_{A\&B \to A}$ of the two-chamber system soon after all particles are in chamber A. As is usually done in classical thermodynamics, we calculate integral (1) along an isothermal compression from state [**gas in volume A&B**] to state [**gas in volume A**] of an ideal gas with equation of state $PV = kNT$ (k is Boltzmann's constant and N the total number of molecules). The compression is isothermal and the internal energy U of the gas is constant. From the first law of thermodynamics $\delta Q = dU + \delta W$, we have $\delta Q = \delta W = p\, dV = kN/V\, dV$, and thus

$$\Delta S_{A\&B \to A} = \int_{V_{A\&B}}^{V_A} \frac{\delta Q}{T} = \int_{V_{A\&B}}^{V_A} \frac{kN}{V} dV$$

$$= kN \ln\left(\frac{V_A}{V_{A\&B}}\right) = -kN \ln 2 < 0 \tag{5}$$

being $V_{A\&B} = 2V_A$.

Actually, consider the above experiment with only 18 molecules in each chamber. In such a case Eq. (4) gives $\langle T \rangle \approx 1$ year. This means that every year, on average, this reduced system violates the second laws by an amount of $|\Delta S| = k \cdot 36 \cdot \ln 2 = 3.44 \times 10^{-22}$ J/K, at the most. Unfortunately, such a violation could hardly be exploited (to produce usable work), not because of its minuteness but because we do not know exactly *when* this violation happens.[2]

Every other known fundamental laws of physics, like those of Newton's mechanics, Einstein's relativity, Maxwell's theory of electromagnetism and even the fundamental laws of quantum mechanics (although quantum mechanics is intimately linked to an intrinsic probabilistic approach to reality, its fundamental laws are not probabilistic) provide an absolute and unconditional prescription on how processes should behave in nature. For instance, Newton's laws tell us that a body on which no forces work undergoes no acceleration; it does not tell us that the body has 'a very big chance' of undergoing no acceleration. Maxwell's theory tells us that two positive charges far removed from any other charge distributions will repel each other and how; not that they will repel each other 'with high probability'. The second law, instead, forbids some processes not absolutely, but only with *very high probability*.

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[1] It is well known that 22.414 l of gas at standard conditions ($T=263.15$ K, $P=1.0235 \times 10^5$ Pa) contain 6.023×10^{23} molecules (Avogadro's Number). Hence, any macroscopic volume of gas we deal with in real life contains no less than 10^{20}–10^{23} molecules.

[2] But, somehow, this is like saying that the laws of physics *forbid* mankind to reach Jupiter's satellite Europa simply because we do not have the required technology yet.

2.1. Maxwell's Demon: a digression

A two-chamber thought experiment, very similar in the spirit to that shown above, dates back to 1867, when Maxwell introduced it for the first time to show that the second law of thermodynamics has only a *statistical validity*. Actually, he made the point more cogent by introducing what it is now known as "Maxwell's Demon" (Fig. 3). In his own words:

… 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 … (Leff & Rex, 2003)

The number of molecules in A and B are the same as at first, but the energy in A is increased and that in B diminished, … and yet no work has been done, only the intelligence of a very observant and neat-fingered being has been employed. Or in short if the heat is the motion of finite portions of matter and if we can apply tools to such portions of matter so as to deal with them separately, then we can take advantage of the different motion of different proportions to restore a uniform hot system to unequal temperatures or to motions of large masses. Only we can not, not being clever enough … (Garber, Brush, & Everitt, 1995)

… I do not see why even intelligence might not be dispensed with and the thing be made self-acting. Moral: The 2nd law of Thermodynamics 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. (Maxwell, 1870)

What is interesting with respect to our previous thought experiment (Fig. 2) is that Maxwell's thought experiment accomplishes a violation of the second law that is also an exploitable
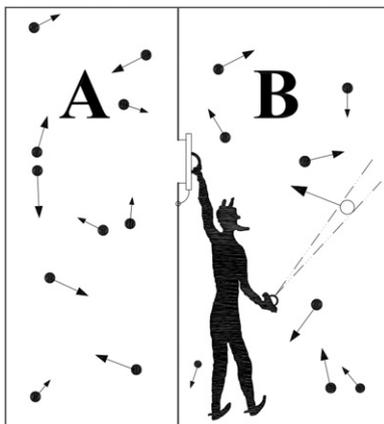
violation, namely one that is able to produce usable work. We have seen, with our reduced gas-in-two-chambers system above, that violation of the second law and exploitable violation of the second law are not the very same thing.

Maxwell's "neat-fingered being" has given rise to an incredibly rich literature over the subsequent decades, which is still ongoing and stronger than ever. Born as a simple and very effective *Gedanken experiment* to elucidate the limits of the second law, almost all the subsequent scholars forgot Maxwell's pristine intention and focused their attention entirely on the evil being, trying to exorcise it, namely trying to show (prove) the impossibility of the Demon to operate in order to save the second law and to preclude the possibility of macroscopic exploitation of such a violation (the generation of usable work).

Smoluchowski, with his one-way valve (Smoluchowski, 1914), and Feynman, with the ratchet and pawl analogue (Feynman, Leigthon, & Sands, 1963), introduced a *non-sentient* version of Maxwell's Demon, using pure physico-mechanical devices without the need of an 'intelligent being' able to 'perceive' velocities, 'see' paths and 'handle' molecules (see the last quotation by Maxwell). They have shown that the thermal fluctuations suffered by these mechanical devices prevent any anti-entropic action, such the sorting of molecules from one vessel to the other.

As a matter of fact, every mechanical device supposed to sort molecules must work at the same absolute temperature of the gas; otherwise, its action may be ascribed to a possible extraction of work from heat reservoirs at different absolute temperatures, like a standard Carnot engine, and this does not count as a 'regular' second law violation. Hence, the mechanical device itself must follow the same canonical distribution function associated with the temperature of its immediate surrounding.

For instance, in the Smoluchowski one-way valve molecules have an average kinetic energy of $\sim kT$ in a given direction, so the valve-trapdoor must be sensitive to energies that high, and preferably lower energies as well. But the trapdoor has the same temperature as the molecules; it is, after all, in contact with them. That means it has fluctuations of kinetic energy of the same size as the molecules; that is, on the size of $\sim kT$. The trapdoor must be sensitive to energies of order kT, and it itself is plagued by fluctuations of order kT. So it is sensitive to random fluctuations, and there will be no correlation between the openings of the trapdoor and the arrival of molecules.

Other researches attempted to investigate the *sentient* version of Maxwell's Demon (probably, the original one), that of intelligently operated devices. Szilard and Brillouin argued that in order to achieve the entropy reduction, the intelligent being must acquire knowledge on molecule's dynamical state (position, velocity) and so must perform a measurement. Thus, they argued that the second law would be saved if the acquisition of knowledge by the Demon came with a compensating entropy cost (Brillouin, 1951; Szilard, 1929).

In more recent years, some researchers (Bennett, Landauer and followers) have claimed that measurements can be performed without entropy costs at all. Instead, they focused their attention exclusively on the process of information erasure, needed by sentient Demon to operate cyclically. All the information gathered and stored by the Demon on the dynamical status of the molecules must be first acquired and then necessarily erased in order to operate cyclically (Bennett, 1982, 1987; Landauer, 1961). According to the information erasure school, any kind of sentient Demon is strictly and absolutely forbidden to violate the second law by the unavoidable entropy cost of the information erasure step, which must be always present in order to make the Demon's operation cyclical. This step provides the Universe with an entropy increase greater than or equal to the alleged entropy reduction operated by the Demon.

Fig. 3. A cartoon depiction of Maxwell's Demon (adapted from Lerner, 1975).

Although the connection between physical entropy and information theory is now widely recognized, its arguments appear to be either circular (themselves typically rely on some version of the second law) or appeal to the existence of new profound laws, which have nothing to do with the fundamental physical principles (classical and quantum mechanical) that govern the behavior of matter (Callender, 2004; Earman & Norton, 1998, 1999; Norton, 2005), and are, in the end, a mere recasting of the second law in the lofty formalism of information theory: not an explanation of it by the known fundamental laws of physics nor a proof of its necessity (Bennett, 2003).

A robust argument against the necessity of information acquisition (measurement) and/or memory erasure entropy costs to defeat Maxwell's Demon goes as follows. Historically, Szilard (1929), Bennett (1982, 1987) and followers have all used the Szilard one-molecule heat engine to illustrate their respective point. The Szilard heat engine works as follows. Initially the entire volume V of a cylinder is available to a single molecule. The first step consists of placing a partition into the cylinder, dividing it into two equal chambers. In step 2 Maxwell's Demon determines which side of a partition the molecule is on, and records this result. In step 3 the partition is replaced by a piston, and the recorded result is used to couple the piston to a load upon which work W is done. The gas pressure move the piston to one end of the container, returning the gas volume to its initial value, V. In the process the one-molecule gas has energy $Q=W$ delivered to it via heat from a constant temperature heat reservoir. After step 3 the gas has the same volume and temperature it had initially. The heat bath, which has transferred energy to the gas, has lower entropy than it had initially. Without some other mechanism, the second law has been violated during the cyclic process.

Szilard and followers (Brillouin[3] and Gabor being the most representative ones) suggested that one may reasonably assume that an amount of entropy is generated during the measurement process by the Demon (in order to know which side of the partition the molecule is on) that restores concordance with the second law. Bennett and followers, instead, argued that the Demon must erase its record on the position of the molecule in order to make the whole process cyclic. Thus, they associated with the erasure step an entropy increase no less than the entropy reduction operated by the Demon.

As a matter of fact, it is not difficult to devise a modified Szilard's heat engine which cyclically works without the need of information acquisition and/or memory erasure. Such an engine is shown in Fig. 4. It is made of a movable cylinder and two pistons (the left one movable and the right one fixed). There is also a partition that can be lowered in the middle of the cylinder and that can slide horizontally on a lowering rod without friction as the cylinder moves. The insertion of the partition involves no work or heat. All the mechanical parts are thought without friction, as has been done extensively in the literature on the subject (more on this later). Initially the entire volume V of a cylinder is available to a single molecule (step A). The behavior of the molecule is described by the equation of state $PV=kT$. Then, the partition is lowered into the cylinder, dividing it into two equal chambers (step A_1). The molecule is trapped in one of these two chambers.

Then, the movable piston is pushed infinitesimally slowly (reversibly) to position B and the one-molecule gas undergoes
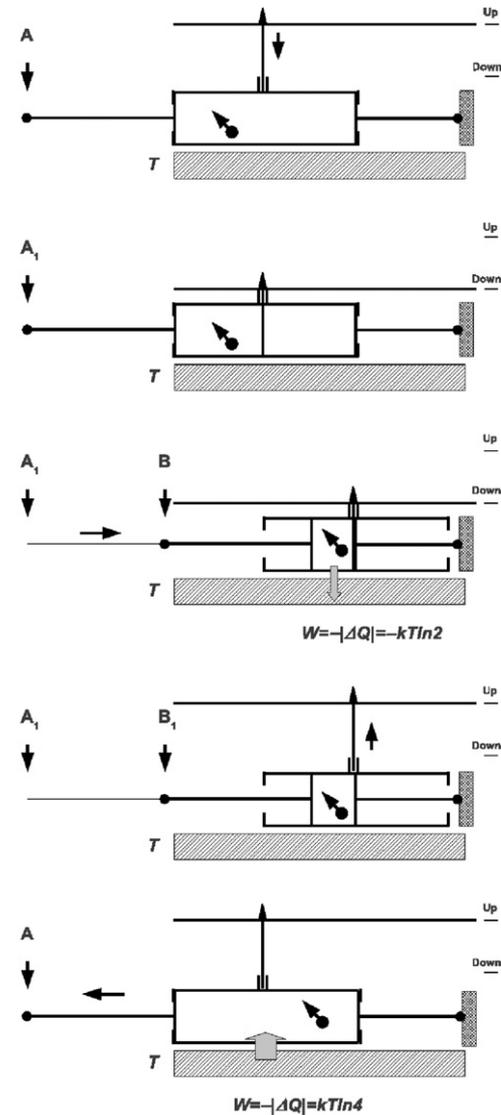

$$W=-|\Delta Q|=-kT\ln2$$

$$W=-|\Delta Q|=kT\ln4$$

Fig. 4. The modified Szilard's heat engine described in the text.

an isothermal compression from $V/2$ to $V/4$. The work $W_{A_1 \to B}$ externally done to the gas is equal to $kT \ln 2$, which is also equal to the heat transferred by the gas to the heat reservoir at temperature T. Note that this part of the cycle is independent of which side of the partition the molecule is on at step A_1, hence we do not need any information acquisition (with subsequent memory erasure). The final position of the movable piston is always at point B, no matter if the molecule is in the right or in the left chamber after step A_1. Besides, the movement of the partition can be mechanically coupled to the cyclic movement of the movable piston, and thus without any need of information acquisition and/or memory erasure to operate the partition itself.

One may complain that the compression procedure depends on whether the molecule is trapped on the left or right. Namely, if the molecule is on the left, the piston moves the whole cylinder first, with its action on the cylinder mediated by the gas pressure. If the molecule is on the right, the piston moves in unimpeded to contact the partition and then compresses the gas. Since the two processes appear to be slightly different, one may wonder that in order to operate the device you have to know which conditions is at hand. This would mean measurement and/or memory erasure. Under a more careful analysis one can easily see that the two processes are not different at all. In both cases there is a first

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[3] In particular, Brillouin (1951) mathematically addressed in explicit way the original form of Maxwell's Demon, namely that of a "neat-fingered being" able to actually see individual molecules. He showed that in order to see the single molecule the Demon should use a (black-body) radiation more energetic (higher temperature) than the black-body radiation of the gas and environment, thus generating a compensating entropy increase.

phase where the device moves unimpeded until the right piston, if the molecule is on the left, or the left piston, if the molecule is on the right, touches the partition (from step A_1 to the midpoint between A_1 and B), and then a second phase in which there is the true gas compression (from the midpoint between A_1 and B to step B). These two phases are physically perceived always in the same way by who/what operates the device: the first half of the compression is always equally 'loose', no matter where the molecule is at the beginning of the process, while the second half is the true gas compression.

At step B_1, the partition is raised and the cycle is completed with an isothermal expansion from $V/4$ to V (with movable piston again in position A). Now, the work $W_{B_1 \rightarrow A}$ made by the gas to the environment is equal to $kT \ln 4$, which is also equal to the heat transferred by the heat reservoir at temperature T to the gas. The net work output W_n over any cycle is then equal to $W_{B_1 \rightarrow A} - W_{A_1 \rightarrow B} = kT(\ln 4 - \ln 2) = kT \ln 2$. Moreover, the entropy variation ΔS of the entire system (engine + reservoir) is equal to $-k \ln 2$.

If we want to save the second law in the above scheme, then some other mechanisms must come into play to prevent the modified Szilard engine from operating. For instance, thermal fluctuations surely afflict the mechanical parts of the engine (pistons, partition and so on) (Earman & Norton, 1999). The pistons must be sensitive to energy of the order of kT, the mean energy of the molecule, and they themselves are plagued by fluctuations of order kT, like the Smoluchowski one-way valve. Actually, if there were no friction, then the device could operate even with arbitrarily massive pistons, partition and cylinder (massive means not instantaneously sensitive to energy of the order of kT). As a matter of fact, without friction even the tiny kick of a single molecule can move a massive piston/cylinder (conservation of linear momentum). But friction cannot be eliminated, even ideally, since thermal fluctuations of the matter along the contact points between the pistons' edge and the cylinder's walls originate an unavoidable friction force that is surely greater than the force imparted by the molecule to the pistons.

But, if such effects afflict our modified Szilard's engine, then the same effects must afflict the original Szilard's engine, being both engines mechanically similar. Hence, the appeal to information acquisition and/or memory erasure entropy costs to defeat Maxwell's Demon in the instantiation of the original Szilard's engine is superfluous. On the other hand, if information acquisition and/or memory erasure entropy costs are strictly necessary to defeat original Szilard's engine, then this means that no other mechanisms are able to prevent its operation. But this last thing would necessarily apply also to our modified Szilard's engine. Thus, our engine would surely violate the second law, since measurement and memory erasure, with their associated entropy costs, do not apply to it, as we saw above. As a logical consequence, measurement and memory erasure entropy costs are again unnecessary to defeat Maxwell's Demon, this time in the instantiation of our modified Szilard's engine.

As a conclusion, the appeal to measurement and memory erasure entropy costs made by Szilard and Bennett within the original Szilard's engine appears to be an arbitrary choice rather than a necessity in defeating Szilard's Demon.

Probably the true reason why non-sentient Demon cannot operate, namely cannot macroscopically violate the second law and create usable work, is the ubiquity of thermal fluctuations and friction in the physical matter, the matter which inevitably constitutes both gas and every passive device conceived to sort molecules in the gas-in-two-chambers scheme.

Fluctuations make the non-sentient Demon ineffective and ultimately Maxwell's thought experiment of the two-chamber vessel with a non-sentient Demon becomes equivalent to our thought experiment (Fig. 2) of the two chambers connected by a wide open hole: macroscopic violation of the second law can be possible *only* by macroscopic statistical fluctuations of molecules between chambers, with or without a sorting Demon.

In addition, every sentient Demon (for instance, like that of Brillouin) which in order to operate needs to acquire information on the molecule (or even to erase memory) necessarily must release (exchange) energy to the gas and the environment: this is equivalent to a Demon which performs work to the system. It is not a canonical Maxwell's Demon, which operates "without expenditure of work", in Maxwell's own words. Thus, there is the strong feeling that every sentient Demon is doubly ineffective in violating the second law in the gas-in-two-chambers scheme: first, because every mechanical part of it, which has to be 'picometric' in order to deal with single molecules, is unavoidably plagued by thermal fluctuations[4] and friction; second, because every energy exchange with the gas required by the measurement process (or even by the memory erasure) may imply a further entropy increase.

2.2. Back to the second law

The critical evaluation of the literature on Maxwell's Demon and, to some extent, of Maxwell's Demon itself are not the main goal of this paper; the interested reader is referred to Leff and Rex (2003), Earman and Norton (1998, 1999), Maroney (2009), Gijsbers (2004) and the references therein.

Rather, our interest is mainly in the epistemological significance of the gas-in-two-chambers scheme (with or without Maxwell's Demon) for the status of the second law.

Given the above, the only logically tenable, legitimate and more basic inference that can be drawn from the gas-in-two-chambers thought experiment (that of Maxwell but, above all, that depicted in Fig. 2 and described before), is **not** that the probability of a macroscopic and exploitable violation of the second law is *always* extremely small (practically zero) and thus the second law is safe, but that:

(i) the second law is *not a necessary law*. There are not known fundamental laws of physics which absolutely forbid its violation and thus it can be macroscopically violated in principle. None of Maxwell's Demon exorcisms provides basic principles and fundamental laws of physics able to absolutely forbid the violation of the second law. There is no exorcism that is not attributable in the end to thermal fluctuations and friction convincingly and beyond a reasonable doubt;

(ii) the probability of a macroscopic and exploitable violation of the second law is extremely small **if** one uses the gas-in-two-chambers scheme or analogues, with or without a sorting Demon. As a matter of fact, thermal fluctuations make every gas-in-two-chambers scheme with a sorting (sentient or non-sentient) Demon equivalent to a gas-in-two-chambers scheme with a wide open hole between the two chambers. Thus, macroscopic violations of the second law are possible only by macroscopic statistical fluctuations of molecules between chambers. And we know that this is statistically highly improbable.

From Maxwell's and our thought experiment one cannot definitively infer that the second law cannot be macroscopically

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[4] In Feynman's own words: 'If we assume that the specific heat of the demon is not infinite, it must heat up. It has but a finite number of internal gears and wheels, so it cannot get rid of the extra heat that it gets from observing the molecules. Soon it is shaking from Brownian motion so much that it cannot tell whether it is coming or going, much less whether the molecules are coming or going, so it does not work.'. Besides, in a recent work Norton (2011) provides a general result which seems to rigorously show the unavoidability of such a limitation.

violated by schemes *different* form the gas-in-two-chambers ones, those for instance not involving gas, liquid or solid atoms and molecules in thermal equilibrium (whose behavior is described by the canonical distribution).

For what concerns the gas-in-two-chambers scheme described before (Fig. 2), the following summary inference chart holds:

(1) Gas spontaneous macroscopic compression in the gas-in-two-chambers scheme	$\Rightarrow$	Macroscopic violation of the second law
	But	
(2) Practical impossibility of gas spontaneous macroscopic compression in the gas-in-two-chambers scheme	$\nRightarrow$	Absolute macroscopic non-violability of the second law
(3) Macroscopic violation of the second law	$\nRightarrow$	Real possibility of gas spontaneous macroscopic compression in the gas-in-two-chambers scheme, *which is actually anything but probable*

Namely, the inability of the gas-in-two-chambers scheme (with or without Maxwell's Demon) to macroscopically violate the second law is *logically* uncorrelated with the actual possibility of second law macroscopic violation.

The inference (3) has been explicitly added since sometime people are overwhelmed by the logical fallacy that if the second law can be somehow macroscopically violated, then this would automatically imply that gas spontaneous compressions in the gas-in-two-chambers scheme would be actually possible. Then, with a sort of 'inverted logic', they argue that being such compressions statistically highly improbable then the second law cannot be macroscopically violated. These two facts, as showed in point (3) of the inference chart, are uncorrelated in such an inference direction.

What we are suggesting is that Boltzman's principle of statistical entropy increase[5] (well represented by the high improbability of spontaneous gas compression) and the macroscopic violation of the second law of thermodynamics can be both true or, better, are not mutually exclusive (see also Duncan, 2002). By the way, Versteegh and Dieks (2011), in a very interesting paper on the Gibbs paradox and the distinguishability of identical particles, point out that the entropy concept in thermodynamics is not completely identical to that in statistical mechanics.

While *necessity* by fundamental physics principles would mean strict inviolability, as far as the known fundamental laws of physics are valid, a possible non-necessary (contingent) nature of the second law, as is clear from the above considerations, leaves the door open for its violability. Obviously, contingency is a necessary but not sufficient condition for violability. Given the actual status of the second law, research aiming at the study of its violability appears to be worthwhile.

3. The quest for violation

Over the past 30 years, an unparalleled number of challenges has been proposed against the status of the second law. During this period, more than 50 papers have appeared in the refereed

scientific literature (Čápek & Sheehan, 2005). Moreover, during the same period three international conferences on the limit of the second law were also held (Sheehan, 2002, 2006, 2011).

Obviously, not all the scholars are willing to acknowledge a respectable status to this line of research. For instance, Gyftopoulos and Beretta (2005) wrote:

If no challenges have been proven valid [so far], what is the motivation for pursuing exploratory research to prove that the second law is invalid? To put our question differently, why people interested in exploratory research do not try to prove that the solar system is neither geocentric nor heliocentric? Similarly why researchers do not try to prove that, in the realm of its validity, Newton's equation of motion is not correct?

The straight answer to this question is that, as argued before, both Newton's laws of mechanics and the heliocentric theory hold a different (epistemological) status with respect to the second law of thermodynamics.

The general class of recent challenges spans classical/standard (Crosignani & Di Porto, 1996, 2001, 2007; Crosignani, Di Porto, & Conti, 2004; D'Abramo, 2010, 2011; Denur, 1981, 1989, 2004, 2007; Gordon, 1981, 1983, 1994, 2004a, 2004b, 2004c), plasma (Sheehan, 1995, 1996; Sheehan & Means, 1998),chemical (Sheehan, 1998, 2000, 2001; Sheehan & Seideman, 2005), gravitational (Sheehan & Glick, 2000; Sheehan, Glick, & Means, 2000, 2002a, 2002b), solid state (Sheehan & Gross, 2006; Sheehan, Wright, & Putnam, 2002, 2005) and quantum physics (Allahverdyan & Nieuwenhuizen, 2000, 2003, 2001, 2004; Berger, 2005, 2007; Bok & Čápek, 2004; Čápek, 1997a, 1997b, 1998, 2001, 2002, 2003; Čápek & Bok, 1998, 1999, 2001, 2002; Čápek & Frege, 2000; Čápek & Mančal, 1999, 2002; Čápek & Tributsch, 1999; Čápek & Sheehan, 2002; Keefe, 2003, 2004, 2005; Nieuwenhuizen & Allahverdyan, 2002; Nikulov & Zhilyaev, 1998; Nikulov, 2001). Some of these approaches appear immune to standard second law defenses and several of them account laboratory corroboration of their underlying physical processes. Others, mainly some classical/standard and gravitational challenges, have been criticized and/or proved faulty beyond any reasonable doubt (see, for example Chardin, 1984; Motz, 1983; Wheeler, 2004).

A thorough description of all these challenges is a quite hard task to accomplish and it is beyond the scope of this paper. The interested reader may find a very detailed review in Čápek and Sheehan (2005) and Sheehan (2008).

From the point of view of direct laboratory testability, the more promising challenges appear to be the solid state ones (Sheehan & Gross, 2006; Sheehan et al., 2002, 2005), together with the challenge posed by thermo-charged capacitors (D'Abramo, 2010, 2011).

3.1. Solid state challenges

Since 2002, two types of solid state devices have been proposed (Čápek & Sheehan, 2005; Sheehan & Gross, 2006; Sheehan et al., 2002, 2005) that basically utilize the electric field energy of an open-gap n–p junction. They are based on the cyclic electro-mechanical discharging and thermal recharging of the electrostatic potential energy intrinsic to the depletion region of a standard solid state n–p junction. The core of their functioning is the shaped junction depicted in Fig. 5.

It consists of two symmetric horseshoe-shaped pieces of n- and p-semiconductor facing one another. At Junction I (J-I), the n- and p-regions are physically connected, while at Junction II (J-II) there is a vacuum gap whose width x_g is small compared to the scale lengths of either the depletion region x_{dr} or the overall device x_{dev}; namely, $x_g \ll x_{dr} \sim x_{dev}$. All the scale lengths are in the *micro-*, *nano-metric* realm.

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[5] A system approaches equilibrium because it evolves from states of lower toward states of higher probability, and the equilibrium state is the state of highest probability.
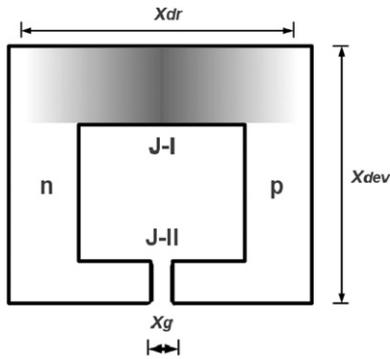
Fig. 5. The core of the solid state challenge. Adapted from Sheehan et al. (2002).

As is well known from solid state physics, a built-in potential V_{bi} forms across the junction J-I, whose numerical value depends on the doping characteristics of the two regions (concentrations of donors and acceptors, intrinsic carrier concentration) and on the environmental temperature (in the present case, room temperature). Its value can be estimated analytically.

This potential is the result of charge diffusion across J-I as soon as the two materials are physically joined. The depletion region is thus the region where, at equilibrium, a balance between bulk electrostatic and diffusive (thermally driven) forces is attained.

It is then claimed that an electric field must exist also in J-II. According to Sheehan et al. (2002, 2005), Sheehan and Gross (2006), and Čápek and Sheehan (2005), the existence of an electric field in the J-II gap at equilibrium can be established either via Kirchhoff's loop rule (conservation of energy) or via path-independence $\oint \mathbf{E} \cdot d\mathbf{l} = 0$. It is argued as follows. Consider a vectorial loop threading the J-I depletion region, the bulk of the device in Fig. 5, and the J-II gap. Since the built-in electric field in the J-I depletion region is unidirectional, there must be a second electric field somewhere else along the loop to satisfy $\oint \mathbf{E} \cdot d\mathbf{l} = 0$. An electric field elsewhere in the semiconductor bulk (other than in the depletion region), however, would generate a current, which contradicts the assumption of equilibrium. Therefore, by exclusion, the other electric field must exist in the J-II gap. Kirchhoff's loop rule establishes the same result. Conservation of energy demands that a test charge conveyed around this closed path must undergo zero net potential drop; therefore, to balance V_{bi} in the depletion region, there must be a counter-potential somewhere else in the loop. Since, at equilibrium, away from the depletion region in the bulk semiconductor there cannot be a potential drop (electric field)—otherwise there would be a non-equilibrium current flow, contradicting the assumption of equilibrium—the potential drop must occur outside the semiconductor; thus, it must be expressed across the vacuum gap J-II.

Because the J-II gap is narrow ($x_g \ll x_{dr}$) and the built-in potential is discontinuous (due to the vacuum gap), there can be large electric fields there, which can be much greater than in the J-I depletion region. As a matter of fact, one can estimate the relative magnitude as follows: the J-II electric field is $\left|\mathbf{E}_{\text{J-II}}\right| \simeq V_{bi}/x_g$, while the average magnitude of the field in J-I is $\left|\mathbf{E}_{\text{J-I}}\right| \simeq V_{bi}/x_{dr}$, thus their ratio scales as $\left|\mathbf{E}_{\text{J-II}}\right|/\left|\mathbf{E}_{\text{J-I}}\right| \sim x_{dr}/x_g \gg 1$.

Through a mathematical treatment of the device, it has been shown (Čápek & Sheehan, 2005; Sheehan et al., 2002) that if some provisos on x_g and x_{dr} are met, then the electrostatic potential energy in J-II (electrostatic energy density times gap volume) is much greater than that in the entire depletion region J-I. Moreover, if the open gap J-II is switched closed (thus becoming a second J-I junction), then such an excess energy is positively released. Most of the free electronic charges on each gap face disperse through and recombine in the J-II bulk.

It is clear that if such a release can be made cyclical through an electro-mechanical nano-apparatus, then this kind of device can exploit the thermally driven diffusion across J-I to produce usable work. Namely, it appears to violate the second law of thermodynamics in the Kelvin–Planck formulation.

Two kinds of such an electro-mechanical apparatus have been proposed and modeled so far (both analytically and numerically), one which uses a Linear Electrostatic Motor (LEM) (Čápek & Sheehan, 2005; Sheehan et al., 2002), and the other using an Hammer and Anvil analogue (Čápek & Sheehan, 2005; Sheehan, 2008; Sheehan & Gross, 2006; Sheehan et al., 2005).

Although the existence of an intense electric field in J-II has been recently put into question on the basis of some heuristic and theoretical arguments (which do not appeal circularly to the validity of the second law, D'Abramo, 2012), micro-metric partial hammer and anvil prototypes have been fabricated and are currently undergoing laboratory tests. The authors report that preliminary results appear to be positive (Sheehan & Wright, 2011).

3.2. Thermo-charged capacitors

Thermo-charged capacitors are vacuum capacitors spontaneously charged harnessing the heat absorbed from a single thermal reservoir at room temperature (D'Abramo, 2010, 2011).

In Fig. 6 a sketched section of a vacuum spherical thermo-charged capacitor is shown. The outer sphere has radius b and it is made of metallic material with relatively high work function ($\phi_{ext} > 1$ eV). The inner sphere has radius a and it is made of the same conductive material as the outer one, but it is coated with a layer of semiconductor Ag–O–Cs, which has a relatively low work function ($\phi_{in} \lesssim 0.7$ eV). In such a case the two thermionic fluxes, from each plate toward the other one, are different, the latter being greater than the former, at least at the beginning of the charging process. The capacitor is shielded by a case and put at room temperature. The case is opaque to every environmental electromagnetic disturbance (natural and man-made e.m. waves, cosmic rays and so on) in order to avoid spurious *photo*-electric emission. Moreover, the outer plate is externally insulated, in order to prevent its outward thermionic emission and the inter-plate space is under extreme vacuum (UHV).

All the electrons emitted by the inner sphere, due to thermionic emission at room temperature, are collected by the outer (very low emitting) sphere, creating a macroscopic difference of potential V. At first, such a process is unbalanced, the flux from
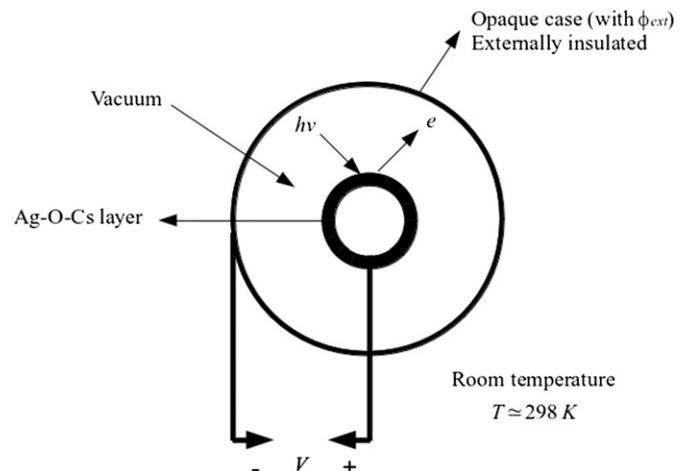

Fig. 6. Scheme of the thermo-charged spherical capacitor. Adapted from D'Abramo (2010).

the inner sphere being greater than that from the outer sphere, but later, with the increase of potential V, the inward and the outward *effective* flux tend to balance each other exactly.

It has been shown (D'Abramo, 2011) that, under conservative conditions, the differential equation which governs the process of thermo-charging is

$$\frac{dV(t)}{dt} = \frac{\pi e b}{2\epsilon_0 c^2}\left(\frac{kT}{h}\right)^3 \left(\overline{\eta}_{in}\int_{(eV(t)+\phi_{in})/kT}^{\infty}\frac{x^2\,dx}{e^x-1}\right.$$

$$\left. -4\overline{\eta}_{ext}\int_{\phi_{ext}/kT}^{\infty}\frac{x^2\,dx}{e^x-1}\right), \qquad (6)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light, e is the electronic charge, k is Boltzmann's constant, h is Planck's constant, $\overline{\eta}_{in}$ is the mean quantum efficiency of thermionic material Ag–O–Cs and $\overline{\eta}_{ext}$ is the mean quantum efficiency of the metallic outer sphere. It can be proved that the radius of the inner sphere a must be equal to half the radius of the outer sphere b in order to have the maximum charging efficiency (faster charging rate). In Fig. 7 the charging profiles for a 20 cm capacitor are shown.

The charging process is a quite straightforward physical mechanism and it appears almost unproblematic. However, during the charging of the device the inner thermionic sphere substantially absorbs heat from the environment and releases this energy to the thermionic electrons. Such electrons fly to the outer sphere and impinge on it with non-zero velocity (since a non-zero fraction of them gathers their kinetic energy from the high energetic tail of the Planck distribution of black-body radiation). When they impinge on the outer sphere, they release their kinetic energy substantially heating the outer sphere. Thus, we are facing a spontaneous process involving an isolated system at uniform temperature (capacitor + environment), in which a part of the system (the inner sphere of the capacitor) absorbs heat at temperature T and transfers a fraction of this heat to the other part of the system (the outer sphere) at the same temperature. This seems to macroscopically violate the second law of thermodynamics in the Clausius formulation. In Maxwell's (1871) own words:

> One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or of pressure without the expenditure of work.
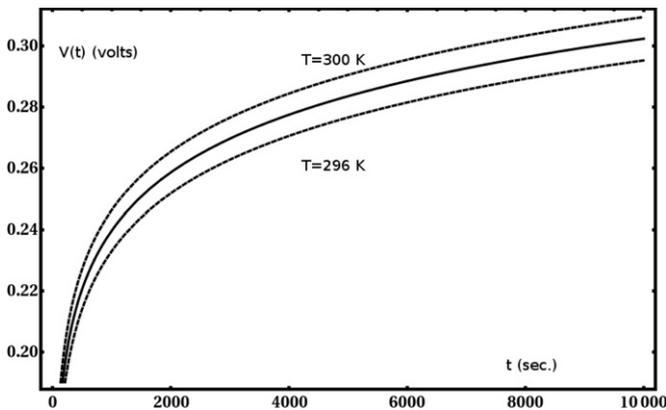

Fig. 7. Thermo-charging profiles $V(t)$ for a spherical capacitor with $\phi_{in}=0.7$ eV, $\phi_{ext}=4.0$ eV, $b=0.2$ m, $T=298$ K, and conservative values of the mean quantum efficiencies $\overline{\eta}_{in}=10^{-5}$ and $\overline{\eta}_{ext}=1$. Charging profiles for $T=300$ K and for $T=296$ K are also shown. Adapted from D'Abramo (2011).

As a matter of fact, if Q_i is the energy absorbed by the inner sphere from the environment, U is the energy stored in the electric field between the spheres ($U=\frac{1}{2}CV^2$, where $C=4\pi\epsilon_0 ab/(b-a)$ is the capacitance of the spherical capacitor), and Q_f is the energy transferred through the flying electrons to the outer sphere as heat (according to the first law of thermodynamics $Q_f+U=Q_i$, thus $Q_i > Q_f$), then the Clausius entropy variation of the whole system, as rough estimate, amounts to

$$\Delta S_{tot} \simeq -\frac{Q_i}{T}+\frac{Q_f}{T} < 0. \qquad (7)$$

In order to make the above result more striking, let us consider the following analogue in classical thermodynamics/mechanics: a boulder of mass m rests at the bottom of a valley, below a hill of height h, all the system at constant temperature T. Suddenly, the boulder spontaneously absorbs an amount Q_1 of heat (energy) from the environment and spontaneously starts to climb the hill at decreasing velocity (since the initial kinetic energy is gradually transformed into gravitational potential energy). Near the top of the hill the boulder hits a sort of wall and then stops. The friction experienced during the hit against the wall lets the boulder release to the environment an amount Q_2 of heat, obviously smaller than Q_1. According to the first law of thermodynamics we have: $Q_1-Q_2=mgh$, where mgh is the gravitational potential energy variation of the boulder from the valley to the top of the hill.

Now, the total Clausius entropy variation is

$$\Delta S_{tot} = -\frac{Q_1}{T}+\frac{Q_2}{T} = -\frac{mgh}{T} < 0. \qquad (8)$$

The behavior of the boulder-environment system is practically the same as that of our electrons-environment system, and it is undoubtedly puzzling from the point of view of the second law of thermodynamics.

Furthermore, the behavior of the electrons just after the emission from the Ag–O–Cs coating is governed by the mechanical/ballistic laws of motion and not by the canonical distribution which describes systems in thermal equilibrium, $p(\mathbf{x},\mathbf{p})=e^{-E(\mathbf{x},\mathbf{p})/kT}/Z$, where $E(\mathbf{x},\mathbf{p})$ is the energy of the system, Z is the normalizing partition function, and the multi-component $\mathbf{x}$ and $\mathbf{p}$ are generalized configuration and momentum coordinates. Hence, the randomizing (disruptive) effect of thermal fluctuations for cases described in Norton (2011) does not appear to apply here.

Concerning the exploitability of such an alleged violation, it has been shown in D'Abramo (2011) that the potential drop V reached during the thermo-charging process is rapidly transferred to the terminal leads of the capacitor (Fig. 6).

The junction between Ag–O–Cs coating material and the inner metallic sphere is a Schottky junction and behaves like a rectifying diode. In principle, such a rectifying behavior could prevent the potential drop V attained within the two concentric spheres from reaching the terminal leads, and thus could forbid any exploitation.

As a matter of fact, any real rectifying junction is not an ideal one, and a tiny reverse leakage current flows through the junction. This reverse leakage current is typically several order of magnitude greater than the thermionic flux within the spheres and allows the transfer of charges and potential drop to the terminal leads (D'Abramo, 2011).

If we short the terminal leads through a resistor R, then it should be possible to exploit the potential drop V, for example generating heat through R (Joule effect). It is possible to show that the power output per unit area of the inner sphere $\mathcal{P}_s$ is given by

$$\mathcal{P}_s = \frac{2\pi e V_s}{c^2}\left(\frac{kT}{h}\right)^3\left(\overline{\eta}_{in}\int_{(eV_s+\phi_{in})/kT}^{\infty}\frac{x^2\,dx}{e^x-1} - 4\overline{\eta}_{ext}\int_{\phi_{ext}/kT}^{\infty}\frac{x^2\,dx}{e^x-1}\right). \qquad (9)$$
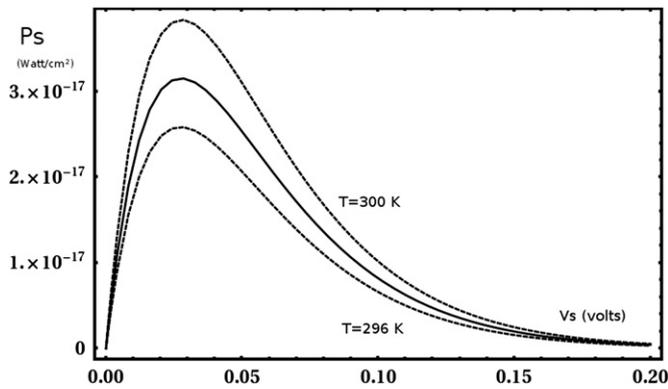
Fig. 8. Power output per unit surface area of the inner sphere, $\mathcal{P}_s$, against voltage drop V_s across resistor R. Power outputs for $T=300$ K and for $T=296$ K are also shown. Adapted from D'Abramo (2011).

V_s is the steady-state potential drop across R and across the capacitor after the current stabilizes. Fig. 8 shows a plot of the above function, in terms of the potential drop V_s.

For the capacitor described in Fig. 6 with $a=10$ cm ($b=20$ cm), we have $P_{max} \approx 10^{-14}$ Watts. This is a quite microscopic output but for laboratory devices, suitably designed for such tests, it should not be a concern, provided that an extremely sensitive, high input impedance electrometer (e.g. Keithley 616, 617 or 6514) is used as measurement equipment.

Moreover, some possible confounding factors, like thermocouple and Thomson effects, can be reduced or canceled out through a proper design of the laboratory devices (D'Abramo, 2011).

One may wonder why such an effect has not been observed before within vacuum tubes. After all, centimeter vacuum tubes have been widely used in electronic devices (phototubes, photomultipliers, radios, TVs, etc.) over a long time before the discovery of silicon (photo)diodes. A possible answer is that the thermocharged capacitor is a ultra-high output impedance source (Teraohms or tens of Tera-ohms) and the effect described here is a really tiny one $\approx 10^{-14}$ Watts, to the point that it may be easily masked by a voltage offset due to electrometer bias current during direct measurements or, if detected, may be confused with other thermionic effects (thermocouple/Thomson effects). Moreover, the commercial vacuum (photo)tubes are not properly designed to measure it. Laboratory tests of thermo-charged capacitors are currently under study.

4. Concluding remarks

In this paper we have argued that we still do not have any fully cogent argument (known fundamental physical laws) to exclude macroscopic violation of the second law of thermodynamics in its classical formulation (Kelvin–Planck and Clausius postulates). Even Landauer's information-theoretic principle seems to fall short of the initial expectations of being the fundamental 'physical' reason of all Maxwell's demons failure. We also described two experimental challenges which have been proposed in recent years and the physics behind them.

However, without unambiguous experimental results (which are currently lacking) it is difficult to say whether these experiments actually challenge or violate the thermodynamic second law, though the theory behind them appears to be sound and as yet unchallenged. Concerning the thermo-charged capacitor challenge, for 'successful violation' we mean production of voltage/current ascribable only to the thermo-charging process beyond any reasonable doubt (and not to other spurious effects like Thomson/Seebeck effects or to measurement interferences).

The impact of any proven success would be understandably enormous from the point of view of basic principles. However, the present author does not believe that, at this stage, such successes would also have profound practical consequences. The power output is so minuscule that it is unthinkable to extract usable work from environmental heat.

Surely, they would shed new light on the possible distinction between thermodynamic entropy (classical thermodynamics) and statistical entropy. As hinted to in Section 2.2, statistical entropy remains unaffected by possible proven successes of these challenges. Even if it turns out that thermodynamic second law is violable, the breakage of a glass, the mixing of milk and coffee and the mixing of two distinct gases, for instance, will always be "irreversible" processes when taken as such (namely, not aided in some way by any of the thermodynamic second law violating devices described above). The direction of such processes always is in the sense of increasing Boltzmann's entropy. In case of future positive results, we are sure that this last embryonic thought about such a distinction will deserve further investigation.

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