Maxwell and a Third Second Law of Thermodynamics

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Abstract

It has long been recognized that there are two distinct laws that go by the name of the Second Law of Thermodynamics. The original says that there can be no process resulting in a net decrease in the total entropy of all bodies involved. A consequence of the kinetic theory of heat is that this law will not be strictly true; statistical fluctuations will result in small spontaneous transfers of heat from a cooler to a warmer body. The currently accepted version of the Second Law is probabilistic: tiny spontaneous transfers of heat from a cooler to a warmer body will be occurring all the time, while a larger transfer is not impossible, merely improbable. There can be no process whose expected result is a net decrease in total entropy.

According to Maxwell, the Second Law has only statistical validity, and this statement is easily read as an endorsement of the probabilistic version. I argue that a close reading of Maxwell, with attention to his use of "statistical," shows that the version of the second law endorsed by Maxwell is strictly weaker than our probabilistic version. According to Maxwell, even the probable truth of the second law is limited to situations in which we deal with matter only in bulk and are unable to observe or manipulate individual molecules. Maxwell's version does not rule out a device that could, predictably and reliably, transfer heat from a cooler to a warmer body without a compensating increase in entropy.

Keywords: Thermodynamics; Second Law of Thermodynamics; James Clerk Maxwell; Maxwell's Demon.

I carefully abstain from asking the molecules which enter where they last started from. I only count them and register their mean velocities, avoiding all personal enquiries which would only get me into trouble.

James Clerk Maxwell, quoted in Garber et al. (1995, p. 19).

1 Introduction: two Second Laws of thermodynamics

It has become a commonplace that there are two distinct version of the Second Law of thermodynamics. The original deems it impossible that there be a transfer of heat from a cooler body to a warmer body without a compensating increase of entropy of some other body (to paraphrase Clausius' formulation).This is in tension with the kinetic theory of heat, which leads us to expect that the thermal agitation of molecules will give rise to fluctuations of temperature and pressure. These fluctuations entail that a gas that is initially at a uniform temperature and pressure can spontaneously develop differences in temperature or pressure—a decrease (however slight) in entropy, which need not be compensated by an increase elsewhere.

What most physicists today accept is something along the lines of,

> Although fluctuations will occasionally result in heat passing spontaneously from a colder body to a warmer body, these fluctuations are inherently unpredictable; there can be no process that will *consistently and reliably* transfer heat from a cooler to a warmer body without producing a compensating increase in entropy elsewhere.

Call this the probabilistic version of the Second Law of thermodynamics.

In the decade 1867–1877, the major figures in the development of the kinetic theory came to accept that the Second Law would have to be modified. It was the reversibility objection, attributed by Boltzmann to Loschmidt, that made it clear to Boltzmann that monotonic non-decrease of entropy of an isolated system could not be a consequence of molecular dynamics alone, and that probabilistic considerations were required. Boltzmann's probabilistic turn of 1877 has been discussed at length elsewhere (see Uffink (2007), Brown et al. (2009)). Reversibility considerations had been a matter of discussion among British physicists for quite some time. On the letter from Maxwell in which the creature that William Thomson (1874) would nickname Maxwell's "demon"[1] was introduced (Dec. 11, 1867) , P.

[1] Thomson attributes the name to Maxwell:

> The definition of a "demon", according to the use of this word by Maxwell, is an intelligent being endowed with free will, and fine enough tactile and perceptive organisation to give him the faculty of observing and influencing individual molecules of matter (Thomson, 1874, p. 441).

But Maxwell says that it was Thomson who gave the creatures this name (Knott, 1911, p. 214).

G. Tait wrote, “Very good. Another way is to reverse the motion of every particle of the Universe and to preside over the unstable motion thus produced” (Knott, 1911, p. 214). The reversibility argument is spelled out in a letter, dated Dec. 6, 1870, from Maxwell to John William Strutt, Baron Rayleigh; Maxwell follows this with an exposition of the demon, and then draws the

> *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 (Garber et al., 1995, p. 205).

Maxwell's demon makes its first public appearance in Maxwell's *Theory of Heat* (1871), in a section entitled, “Limitation of the Second Law of Thermodynamics.”

Gibbs' recognition of the probabilistic nature of the Second Law occurs in 1875. His statement occurs in the context of a discussion of the mixture of distinct gases by diffusion, with which there is associated an increase of entropy, called the *entropy of mixing.*

> when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any external influence, than there is of the separation of a homogeneous gas into the same two parts into which it as once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability (Gibbs 1875, p. 229; 1961, p. 167).

It is one thing to acknowledge that, given artificial and contrived initial conditions, such as the reversal of all velocities, or those produced by the manipulations of a demon, violations of the Second Law could be produced. This is enough to show that the Second Law cannot be a consequence of molecular dynamics alone. Such considerations leave it open the possibility that such conditions would, in the normal course of things, be so improbable that they would expected to occur very rarely if at all. Maxwell went a step further; he asserted that, on small enough scales, the Second Law will be continually violated.

> If we restrict our attention to any one molecule of the system, we shall find its motion changing at every encounter in a most irregular manner.
>
> If we go on to consider a finite number of molecules, even if the system to which they belong contains an infinite number, the average properties of this group, though subject to smaller variations than those of a single molecule, are still every now and then deviating very considerably from the theoretical mean of the whole system, because the molecules which form the group do not submit their procedure as individuals to the laws which prescribe the behaviour of the average or mean molecule.
>
> Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to

> a real body. As the number of molecules in the group is increased, the deviations from the mean of the whole become smaller and less frequent; and when the number is increased till the group includes a sensible portion of the body, the probability of a measurable variation from the mean occurring in a finite number of years becomes so small that it may be regarded as practically an impossibility.
>
> This calculation belongs of course to molecular theory and not to pure thermodynamics, but it shows that we have reason for believing the truth of the second law to be of the nature of a strong probability, which, though it falls short of certainty by less than any assignable quantity, is not an absolute certainty (Maxwell 1878b, p. 280; Niven 1965, pp. 670–71).

The Second Law of thermodynamics, as originally conceived, must be acknowledged to be false, as Maxwell was perhaps the first to perceive. A plausible successor to it is the probabilistic version. Maxwell, also, thought that a suitably limited version of the Second Law could be correct. Some of what he says about the Second Law suggests the probabilistic version. As we shall see, this doesn't fit with a closer reading of his remarks; the limitation Maxwell endorses is somewhat different.

2 A third version of the Second Law

For Maxwell, the truth of the Second Law is "a statistical, not mathematical, truth" (1878b, p. 280). In a letter to Tait he wrote that the chief end of a Maxwell demon is to "show that the 2nd Law of Thermodynamics has only a statistical certainty" (quoted in Knott 1911, p. 215). To a modern reader, used to the idea that statistics and probability theory are intimately intertwined, there may seem to be no discernible difference between a statistical version of the Second Law and a probabilistic one. Indeed, Maxwell has been read as employing his demon in the service of a probabilistic version of the Second Law. For example, Earman and Norton write,

> Maxwell conceived of the Demon as a helpful spirit, assisting us to recognise most painlessly that the Second Law of thermodynamics can hold only with very high probability, apparently in the sense that there is a very small subclass of thermodynamic systems that assuredly reduce entropy (Earman and Norton, 1998, p. 436).

If the demon is meant to illustrate the fact that the Second Law can only hold with high probability, then, it must be admitted, the example is not well chosen. As Maxwell himself pointed out, statistical fluctuations will produce violations of the original version of the Second Law, without the help of a demon. The passage of faster molecules from one side of a container to the other through the demon's trap door will happen occasionally, without the presence of the demon to close it to block unwanted passages. What the demon does is build up a substantial difference in temperature by selectively accumulating fluctuations that occur without its intervention. So, the demon does not help us see that the original Second Law will be violated; rather, it exploits microscopic violations to build up macroscopic ones. Equally puzzling is the notion that the demon helps us see that the Second Law will hold with high probability; in the presence of the demon, large entropy decreases are not improbable, but virtually certain. Earman and Norton's take on this seems to be that, though, in the presence of a system that acts as a Maxwell demon, entropy will assuredly be reduced, such systems are rare, so that we can expect thermodynamic behaviour from most systems. But in none of Maxwell's discussions does Maxwell say anything about the prevalence, or lack thereof, of demons in nature.

If the probabilistic reading is not what was meant, what *did* Maxwell mean when he said that the demon's chief end was to show that the Second Law has only a statistical certainty? In order to understand this, it is essential to understand what the word "statistical" meant, for Maxwell. The word "statistics" has its origin in the Italian *statista* (statesman), and originally referred to a collection of facts of interest to a statesman. By the nineteenth century the word had come to be applied to systematic compilation of data regarding population and economic matters (Hald, 1990, pp. 81–82), and this would have been the primary meaning of the word for Maxwell's readers.

In 1885, in his address to the Jubilee Meeting of the Statistical Society of London, the Society's president, Rawson W. Rawson, defined statistics as

> the science which treats of the structure of "human society," *i.e.*, of society in all its constituents, however minute, and in all its relations, however complex; embracing alike the highest phenomena of education, crime, and commerce, and the so-called "statistics" of pin-making and London dust bins (Rawson, 1885, p. 8).

There is no suggestion in Rawson's address that statistics and probability theory are closely interconnected, though he does note that "mathematical principles of investigation are available, and, the more closely these are applied, the nearer will be the approach to mathematical precision in the results" (p. 9). This is a symptom of the degree to which the field has been transformed; imagine the current president of the Royal Statistical Society (as it is now known) reminding its membership that mathematical methods are available!

Although there were, of course, mathematicians who were at the time applying probability theory in the field of statistics, this was not yet the dominant approach.

> In the social sciences ... the successful use of probability-based statistical methods did not come quickly... But beginning in the 1880s there was a notable change in the intellectual climate... (Stigler, 1986, p. 239).

Writing in the 1870s, Maxwell could not have assumed that his readers would associate the word "statistical" with considerations of probability.

In a lecture delivered to the British Association for the Advancement of Science (1873), Maxwell discussed the introduction of the statistical method into physics.

> As long as we have to deal only with two molecules, and have all the data given us, we can calculate the result of their encounter; but when we have to deal with millions of molecules, each of which has millions of encounters in a second, the complexity of the problem seems to shut out all hope of a legitimate solution.
>
> The modern atomists have therefore adopted a method which is, I believe, new in the department of mathematical physics, though it has long been in use of the section of Statistics. When the working members of Section F [the statistical section of the BAAS] get hold of a report of the Census, or any other document containing the numerical data of Economic and Social Science, they begin by distributing the whole population into groups, according to age, income-tax, education, religious belief, or criminal convictions. The number of individuals is far too great to allow of their tracing the history of each separately, so that, in order to reduce their labour within human limits, they concentrate their attention on a small number of artificial group. The varying number of individuals in each group, and not the varying state of each individual, is the primary datum from which they work.
>
> This is, of course, not the only method of studying human nature. We may observe the conduct of individual men and compare it with that conduct which their previous character and their present circumstances, according to the best existing theory, would lead us to expect (Maxwell 1873, p. 440; Niven 1965, 373–74).

To adopt the statistical method in physics means to eschew the attempt to follow the trajectories of individual molecules—"avoiding all personal enquiries" of molecules—and it is only insofar as we do so that the Second Law has any validity. It is not just that it is not exceptionless. For Maxwell, even a probabilistic version holds only so long as we are in a situation in which molecules are dealt with only *en masse*. This is the limitation of which he speaks, in the section of *Theory of Heat* that introduces the demon to the world.

> 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 pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving the separate molecules of which they are made up. But 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 still as essentially as finite as our own, would be able to do what is at present impossible to us. For

> we have seen that the 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 ones 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.
>
> This is only one of the instances in which conclusions which we have drawn from our experience of bodies consisting of an immense number of molecules may be found not to be applicable to the more delicate observations and experiments which we may suppose made by one who can perceive and handle the individual molecules which we deal with only in large masses.
>
> In dealing with masses of matter, while we do not perceive the individual molecules, we are compelled to adopt what I have described as the statistical method of calculation, and to abandon the strict dynamical method, in which we follow every motion by the calculus (Maxwell, 1871, pp. 308–309).

Note that there is in this no hint that there might be some principle of physics that precludes the manipulations of the demon, or constrains it to dissipate sufficient energy that the net change of entropy it produces is positive. Moreover, Maxwell leaves open that the requisite manipulations might become technologically possible in the future—the demon does what is *at present* impossible for us. What Maxwell is proposing, as a successor to the Second Law, is strictly weaker than the probabilistic version. For Maxwell, even the probabilistic version is limited in its scope—it holds only in circumstances in which there is no manipulation of molecules individually or in small numbers.

It had long been noted that, though the behaviour of individual humans might be hard to be predict, there are statistical regularities at the population level. So, too, says Maxwell, there are statistical regularities in physics.

> The data of the statistical method as applied to molecular science are the sums of large numbers of molecular quantities. In studying the relations between quantities of this kind, we meet with a new kind of regularity, the regularity of averages, which we can depend upon quite sufficiently for all practical purposes, but which can make no claim to that character of absolute precision which belongs to the laws of abstract dynamics (Maxwell 1873, p. 440; Niven 1965, p. 374).

It is this that he means when he says that the Second Law is a statistical regularity. "The truth of the second law is ... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules, and we can never get hold of a single molecule" (Maxwell 1878b, p. 279; Niven 1965, p. 670).

There is, of course, a relation between a probabilistic version of the Second Law, and a restriction of its scope to circumstances in which molecules are dealt with *en masse*, rather than individually. As Maxwell points out, measurable thermodynamic quantities are averages over many molecular quantities; if the molecular quantities exhibit fluctuations that are probabilistically independent of each other, they will tend to be washed out as the number of molecules considered is increased. Thus the probabilistic version predicts that large deviations from the original version of the Second Law will become overwhelmingly improbable when macroscopic numbers of molecules are involved, and so it shares with Maxwell's version the conclusion that the original version will be observed to hold under ordinary conditions of observation of macroscopic phenomena. This helps to explain why Maxwell has been taken to be advocating the probabilistic version widely accepted today.

Though a number of writers have attributed the probabilistic version of the Second Law to Maxwell—the quotation from Earman and Norton, above, is not atypical—it should be noted that Stephen Brush, in his masterful study of the development of the kinetic theory, does not. Brush correctly notes that the lesson Maxwell draws from the demon is that "the Second Law ... 'has only a statistical certainty'—it is valid only as long as we consider very large numbers of molecules which we cannot deal with individually." Brush adds,

> It must not be assumed that "statistical" here implies randomness at the molecular level, for it is crucial to the operation of the Maxwell Demon that he be able to observe and predict the detailed course of motion of a single molecule (Brush, 1976, p. 589).

Maxwell's interpretation of the Second Law, Brush notes, "is statistical rather than stochastic" (Brush, 1976, p. 593).

Owen Maroney, also, clearly distinguishes Maxwell's view from the probabilistic version. The operation of Maxwell's demon is

> simply a matter of scale and the statistical nature of the second law not probabilistic, but due to our inability to discriminate the exact state of a large number of particles (similar to our inability to exploit Loschmidt's reversibility objection). This leaves open the possibility of a device which could discriminate fluctuations in individual atomic velocities and it is not clear that any probabilistic argument would prevent work being extracted from this (Maroney, 2009).

3 The reality of fluctuations: Brownian motion

Maxwell had sufficient confidence in the molecular theory that, when it turned out that the theory entailed violations of an empirically well-established law of physics—the Second Law of thermodynamics—he embraced the consequence, and accepted the reality of such violations. Maxwell has been vindicated; the fluctuations predicted by molecular theory are observable, most readily in the erratic dance of small particles suspended in liquid called Brownian motion, which we now attribute to statistical fluctuations in pressure.

The French physicist Léon Gouy, in a paper on Brownian motion, drew much the same conclusion about the limitation of the Second Law as Maxwell did. After describing a ratchet-wheel mechanism that (if it worked as advertised[2]), would convert Brownian motion into useful work, Gouy wrote,

> This mechanism is clearly unrealisable, but there is no theoretical reason to prevent it from functioning. Work could be produced at the expense of the heat of the surrounding medium, in opposition to Carnot's principle. ... this principle would then be exact only for the gross mechanisms that we know how to make, and it would cease to be applicable when the *receptor* organ has dimensions comparable to 1 micron (Gouy 1888, p. 564; tr. Brush 1976, p. 670).

One person's *modus ponens* is another person's *modus tollens.* For Poincaré, the fact that the kinetic theory entailed violations of the Second Law was a mark against the kinetic theory, rather than grounds for believing the Second Law to be continually violated at the molecular level. In an 1893 article published in the *Revue de Métaphysique et de Morale*, Poincaré applied his recurrence theorem to the kinetic theory. If thermal phenomena admit of a mechanical explanation, then the theorem applies, and any system will eventually return to a state arbitrarily close to its initial state. This, according to Poincaré, is in contradiction to experience.

> I do not know if it has been remarked the English kinetic theories can extricate themselves from this contradiction. The world, according to them, tends at first toward a state where it remains for a long time without apparent change; and this is consistent with experience; but it does not remain that way forever, if the theorem cited above is not violated; it merely stays there for an enormously long time, a time which is longer the more numerous are the molecules. This state will not be the final death of the universe, but a sort of slumber, from which it will awake after millions of millions of centuries.
>
> According to this theory, to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of Maxwell's demon; it will suffice to have a little patience (Poincaré 1893, p. 536; tr. Poincaré 1966, p. 206).

Poincaré remained hesitant about accepting that the Second Law is violated even in the face of Gouy's investigation of Brownian motion. One place in which he discusses this is in Chapter 10 of *Science and Hypothesis.* There he expresses skepticism about the prospects of a mechanical explanation of irreversible phenomena.

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[2]Gouy's mechanism is not different in its essentials from the mechanism analyzed by Feynman (1963, Ch. 46).

> A strictly mechanical explanation of these phenomena has also been sought, but, owing to their nature, it is hardly likely that it will be found. To find it, it has been necessary to suppose that the irreversibility is but apparent, that the elementary phenomena are reversible and obey the known laws of dynamics. But the elements are extremely numerous, and become blended more and more, so that to our crude sight all appears to tend towards uniformity—*i.e.* all seems to progress in the same direction, and that without hope of return. The apparent irreversibility is therefore but an effect of the law of great numbers. Only a being of infinitely subtle senses, such as Maxwell's demon, could unravel this tangled skein and turn back the course of the universe.
>
> This conception, which is connected with the kinetic theory of gases, has cost great effort and has not, on the whole, been fruitful; it may become so (Poincaré, 1952, pp. 178–179).

It is in light of this skeptical attitude that we should read the paragraph that follows it.

> Let us notice, however, the original ideas of M. Gouy on the Brownian movement. According to this scientist, this singular movement does not obey Carnot's pronsiple. The particles which it sets moving would be smaller than the meshes of that tightly drawn net; they would thus be ready to separate them, and thereby to set back the course of the universe. One can almost see Maxwell's demon at work.

Note that, though Gouy's ideas are "original," Poincaré stops short of endorsing them. It is according to Gouy (but not, it would seem, to Poincaré), that Brownian motion violates the Second Law. In light of the skepticism expressed earlier about the kinetic theory, the last sentence of the quoted paragraph sounds a bit sardonic.

In his 1904 St. Louis lecture, Poincaré again discussed the kinetic theory, irreversibility, and Gouy's views on Brownian motion, and again stopped short of endorsing Gouy's conclusion that in Brownian motion we observe a violation of the Second Law.[3]

> If physical phenomena were due exclusively to the movements of atoms whose mutual attraction depended only on distance, it seems that all these phenomena would be reversible ... On this account, if a physical phenomenon is possible, the inverse phenomenon should be equally so, and one should be able to reascend the course of time.
>
> But it is not so in nature, and this is precisely what the principle of Carnot teaches us; heat can pass from the warm body to the cold body; it is impossible afterwards to make it reascend the inverse way and reëstablish differences of temperature which have been effaced.

[3]The bulk of this lecture appears as Ch. VIII of *La Valeur de la Science*. See Poincaré (1913b, pp. 303-305).

> Motion can be wholly dissipated and transformed into heat by friction; the contrary transformation can never be made except in a partial manner (Poincaré, 1905, pp. 608–609).

Poincaré then explains the position of Maxwell, Boltzmann, and Gibbs, that such a reversal is not ruled out by physics but is only practically impossible.

> For those who take this point of view, the principle of Carnot is only an imperfect principle, a sort of concession to the infirmity of our senses; it is because our eyes are too gross that we do not distinguish the elements of the blend; it is because our hands are too gross that we cannot force them to separate; the imaginary demon of Maxwell, who is able to sort the molecules one by one, could well constrain the world to return backward. Can it return of itself? That is not impossible; that is only infinitely improbable (p. 609).

Poincaré is not among those who take this point of view; rather, he dismisses as theoretical the reservations about the Second Law stemming from the kinetic theory.

Brownian motion, however, raises the possibility of an observable, not merely a theoretical, violation of the Second Law. It had been suggested that the observed motion were temporary, due to inequalities of temperature created by the microscope's light source.

> M. Gouy ... saw, or thought he saw, that this explanation is untenable, that the movements become more brisk as the particles are smaller, but that they are not influenced by the mode of illumination.
>
> If, then, these movements never cease, or rather are reborn without ceasing, without borrowing anything from an external source of energy, what ought we to believe? To be sure, we should not renounce our belief in the conservation of energy, but we see under our eyes now motion transformed into heat by friction, now heat changed inversely into motion, and that without loss since the movement lasts forever. This is contrary to the principle of Carnot.
>
> If this be so, to see the world return backward, we no longer have need of the infinitely subtle eye of Maxwell's demon; our microscope suffices us (p. 610).

His discussion is couched in the subjunctive mood. He is not convinced that Gouy is right that the motions are unceasing; his discussion if about what we *would* conclude were to accept that they are. His attitude towards the kinetic theory remains reserved.

> Among the most interesting problems of mathematical physics, it is proper to give a special place to those relating to the kinetic theory of gases. Much has already been done in this direction, but much still remains to be done. This theory is an eternal paradox. We have reversibility in the premises and irreversibility in the conclusions; and between the two an abyss. Statistic considerations, the law of great numbers, do they suffice to fill it? Many points still remain obscure

> ... In clearing them up, we shall understand better the sense of the principle of Carnot and its place in the *ensemble* of dynamics, and we shall be better armed to interpret properly the curious experiment of Gouy, of which I spoke above (pp. 617–618).

It was Perrin's work, yielding agreeing measurements of Avogadro's number from several disparate phenomena, that convinced many of the reality of atoms (see Nye 1972 for the history). The same is true of Poincaré, though, interestingly, he at first retained his reserved attitude, even in light of Perrin's work.

Poincaré discussed Perrin's work in a lecture (Poincaré, 1912a) delivered in the last year of his life, on March 7, 1912.[4] Though he is struck by the concordance of the counts of atoms derived from multiple independent sources, he stops short of endorsing their reality; "that is not to say, that we see the atoms" (Poincaré, 1913c, p. 60).

> we are far from seeing the end of the struggle between these two ways of thinking, that of the atomists, who believe in the existence of ultimate elements, of which finite, but very large, combinations suffice to explain the various aspects of the universe, and that of the partisans of the continuous or the infinite. This conflict will last as long as long as one pursues Science ... (p. 67).

Poincaré expresses a considerably more positive attitude in another lecture delivered just one month later, on April 11, 1912, at the annual meeting of the Société francaise de Physique, at which Perrin was also present and lectured on his results

> The kinetic theory of gases has acquired, so to speak, unexpected props. New arrivals have modeled themselves upon it exactly; these are on the one side the theory of solutions and on the other the electronic theory of metals... The parallelism is perfect and can pursued even to numerical coincidences. In that way, what was doubtful becomes probable; each of these three theories, if it were isolated, would seem to be merely an ingenious hypothesis, for which it would be possible to substitute other explanations nearly as plausible. But, as in each of the three cases a different explanation would be necessary, the coincidences which have been observed could no longer be attributed to chance, whereas the three kinetic theories make these coincidences necessary. Besides, the theory of solutions leads us very naturally to that of the Brownian movement, in which it is impossible to consider the thermal disturbance as a figment of the imagination, since it can be seen directly under the microscope.
>
> The brilliant determinations of the number of atoms computed by Mr. Perrin have completed the triumph of atomism. What makes it all the more convincing are the multiple correspondences between results obtained by entirely different processes (Poincaré 1912b, p. 348; tr. Poincaré 1963, p. 90).

[4]For the dates of this lecture and of Poincaré (1912b), see Auffray (2005, p. 232).

"The atom of the chemist," Poincaré proclaimed, "is now a reality" (Poincaré 1912b, p. 349; 1963, p. 91).

Now that Poincaré has accepted the explanation of Brownian motion as due to thermal agitations of the molecules of the surrounding fluid, gone are the sardonic references to Maxwell's demon. Interestingly, though it follows from his earlier discussion that we should, in light of this, cocnlude that the second law is violated, Poincaré does not explicitly draw this conclusion.

4 Work, heat, and entropy as anthropocentric concepts

There are two way in which energy can be transferred from one system to another: it can be transferred as heat, or else one system can do work on the other. The Second Law of Thermodynamics requires, for its formulation, a distinction between these two modes of energy transfer. In Clausius' formulation,

> Heat cannot pass from a colder body to a warmer body without some other change connected with it occurring at the same time.[5]

To see that this hangs on a distinction between heat and work, note that it becomes false if we don't specify that the energy is transferred as heat. It is not true that energy cannot be conveyed from a cooler body to a warmer body without some other change connected with it: if two gases are separated by an insulating movable piston, the gas at higher pressure can compress—that is, do work on— the gas at lower pressure, whatever their respective temperatures.

The Kelvin formulation of the Second Law is,

> It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects (quoted in Uffink (2001, p. 327)).

This statements does *not* say that we cannot cool a body below the temperature of the coldest surrounding objects. Refrigerators are possible. The difference is: though we can derive mechanical effect—that is, do work— by extracting heat from a hotter body, using some of the energy to do work, and discarding the rest into a cooler reservoir, extraction of heat from a body that is already cooler than any body that might be used as a reservoir requires the opposite of deriving mechanical effect: it requires us to use up some energy that could have been used for mechanical effect, in order to effect the transfer. Thus the Kelvin

[5] "Es kann nie Wärme aus einem kälteren Körper übergehen, wenn nicht gleichzeitig eine andere damit zusammenhängende Aenderung eintritt." Quoted by Uffink (2001, p. 333).

statement, also, requires a distinction between deriving mechanical effect from a body and extracting heat from it.

What is this distinction? On the kinetic theory of heat, when a body is heated, the total kinetic energy of its molecules is increased, so, for body A to heat body B, parts of A must interact with parts of B to change their state of motion. When A does work on B, it is again the case that parts of A act on parts of B to change their state of motion. The difference is: in heat transfer, energy is transferred to the parts of the body in a haphazard way, which cannot be tracked, and which, as a result, cannot be wholly recovered as work.

Put this way, the distinction seems to rest on anthropocentric considerations. This is, in fact, Maxwell's conclusion; "we have only to suppose our senses sharpened to such a degree that we could trace the motions of molecules as easily as we now trace those of large bodies, and the distinction between work and heat would vanish, for the communication of heat would be seen to be a communication of energy of the same kind as that which we call work" (1878b, p. 279). And in the concluding paragraph of his *Encyclopedia Brittanica* article on "Diffusion," he wrote,

> Available energy is energy which we can direct into any desired channel. Dissipated energy is energy we cannot lay hold of and direct at pleasure, such as the energy of the confused agitation of molecules which we call heat. Now, confusion, like the correlative term order, is not a property of material things in themselves, but only in relation to the mind which perceives them. A memorandum-book does not, provided it is neatly written, appear confused to an illiterate person, or to the owner who understands thoroughly, but to any other person able to read it appears to be inextricably confused. Similarly the notion of dissipated energy could not occur to a being who could not turn any of the energies of nature to his own account, or to one who could trace the motion of every molecule and seize it at the right moment. It is only to a being in the intermediate stage, who can lay hold of some forms of energy while others elude his grasp, that energy appears to be passing inevitably from the available to the dissipated state (Maxwell 1878a, p. 221; Niven 1965, p. 646).

If heat and work are anthropocentric concepts, then perforce so is entropy. The entropy difference between two equilibrium states of a system is given by

$$\Delta S = \int \frac{đQ}{T},$$

where the integral is taken over any quasistatic process joining the two states, and $đQ$ is the increment in heat absorbed from the system's environment. Thus, on Maxwell's view, not only is the validity of the Second Law of thermodynamics agent-relative; so are the very concepts required to state it.

Maxwell bases his conclusion that the distinction between available and dissipated energy is agent-relative on considerations of the entropy of mixing, which, as we have seen above, was also the context of Gibbs' remark about the probabilistic character of the Second Law. Consider a container with two sub-compartments, of volume V_1 and V_2, respectively, containing samples of gas at the same temperature and pressure. The partition is removed, and the gases from the two subcompartments are allowed to diffuse into each other. Has there been an increase of entropy, or not?

Maxwell gives the now standard answer, that, if the gases are the same, there is no entropy increase, but, if they are distinct, then there is an increase of entropy equal to the sum of the entropy associated with the expansion of one gas from the volume V_1 to the volume $V_1 + V_2$, plus the entropy associated with the expansion of the other gas from V_2 to $V_1 + V_2$. If the gases are distinct, then the irreversible diffusion of the gases into the larger volume is a lost opportunity to do work.

> Now, when we say two gases are the same, we mean that we cannot distinguish the one from the other by any known reaction. It is not probable, but it is possible, that two gases derived from different sources, but hitherto supposed to be the same, may hereafter be found to be different, and that a method may be discovered of separating them by a reversible process (Maxwell 1878a, p. 221; Niven 1965, pp. 645–646).

It is this that motivates Maxwell's view that heat, work, and entropy are agent-relative; they have to do with *our* ability to manipulate things. An agent who saw no way to separate two gases would not regard their interdiffusion as a lost opportunity to do work, an increase in entropy. If we are in possession of such a means—say, a membrane permeable to one gas and not to the other[6]— then we can connect the initial and final states by a reversible process in which each gas expands, raising a weight, while absorbing heat from a reservoir. We then say that the gas has increased its entropy, while decreasing the entropy of the reservoir. But for a demon that could keep track of the motions of individual molecules, there would be no difference in kind between the raising of the weight and the transfer of heat, and there would again be no increase in entropy of the gas.

A similar view has, in more recent years, been championed by E.T. Jaynes, who expresses his view as "Entropy is an anthropomorphic concept."

> If we work with a *thermodynamic* system of n degrees of freedom, the experimental entropy is a function $S_e(X_1 \cdots X_n)$ of n independent variables. But the *physical* system has any number of additional degrees of freedom X_{n+1}, X_{n+2}, etc. We have to understand that these additional degrees of freedom are not to be tampered with during the experiment on the n degrees of interest; otherwise one could easily produce apparent violations of the second law (Jaynes 1965, p. 398; Jaynes 1989, p. 86).

Jaynes proposes his own modification of the Second Law.

[6]As Daub (1969, p. 329) points out, the device of a membrane permeable to one gas but not the other, now a staple of textbook expositions, dates back to Boltzmann (1878).

> the correct statement of the second law is not that an entropy decrease is impossible in principle, or even improbable; rather that it cannot be achieved reproducibly by manipulating the macrovariables $\{X_1, ..., X_n\}$ that we have chosen to define our macrostate (Jaynes, 1992, p. 10).

Though not identical to Maxwell's version, it is in such the same spirit. The variables we use to define the macrostate will typically be those whose values we can measure and manipulate, and as such will typically be averages over large numbers of of molecular variables. Jaynes' version says that, as long as our manipulations are restricted to these, we will not be able to reliably produce a decrease in entropy.[7]

5 Exorcising the Demon?

As mentioned, most contemporary physicists believe in something like the probabilistic version of the law. If this is correct, then no device can be constructed that could perform the manipulations requisite for the demon to reliably produce an entropy decrease and harness it to do useful work. Maxwell's version, on the other hand, leaves it open that this might someday be technologically feasible, it is only "at present impossible to us."

Suppose there were an advocate of Maxwell's viewpoint who was familiar with the developments in physics since Maxwell's time. What might one say to a modern Maxwell to convince him that such a device not only has not, but could not be constructed?

A reply that the Second Law is a well-confirmed inductive generalization would not be persuasive. Our modern Maxwell could reply that observations so far have been restricted to situations that involve no manipulations of molecules for the express purpose of creating entropy decrease. That something has never been observed is not a good argument that it is not technologically feasible. A convincing argument would have to derive the probabilistic Second Law from some principle for which we can provide independent grounds.

There is a vast literature that attempts to do just this (see Leff and Rex (2003) for an overview, some of the key papers, and an extensive bibliography). There are two main avenues of approach. One, pioneered by the work of Smoluchowski, consists of careful analysis of devices that *prima facie* might seem to be able to function as Maxwell demons, to show that this appearance is an illusion due to neglect of thermal fluctuations in some part of the mechanism. The other avenue employs information-theoretical concepts in an endeavour to locate an unavoidable dissipation of energy either in the act of information acquisition, or in information processing. Along this avenue, the approach that seems to find most favour currently invokes Landauer's Principle, which alleges that erasure of a record that represents n bits of information inevitably results in a minimum average entropy increase of $n\, k \ln 2$.

The reason that Gouy's ratchet mechanism seems *prima facie* to be a device that reliably converts heat from the surrounding fluid wholly into work is that we often, in our

[7] Jaynes arrives at this position via a close reading of Gibbs (1875). The view, as in Maxwell, is motivated by consideration of the entropy of mixing.

analysis of machines, ignore small amounts of heat produced within the mechanism, just as we typically ignore microfluctuations in temperature and pressure. In the unfamiliar setting of attempts to construct a machine that exploits microfluctuations to do useful work, it is essential to pay attention to matters that with warrant we neglect in ordinary settings. This is what makes analyses such as Feynman's analysis of the ratchet-machine valuable. If we accept the probabilistic law, we know that the ratchet-machine must produce waste heat, but it may not be obvious where. Feynman reminds us that a ratchet, to work, must involve damping of the pawl; an elastic pawl that bounces up and down on its ratchet-wheel does not fulfill its function. Damping is the conversion of motion into heat, which raises the temperature of the pawl or its surroundings. Feynman's analysis permits us to see what initially might look like a viable demon-mechanism as a Carnot heat engine, which absorbs heat from one reservoir, uses part of it to do work, and dissipates the remainder into a reservoir at a lower temperature.

Feynman presents his analysis, not as a defense of the Second Law, but a way to understand what is happening physically. Other exorcisms purport to provide support for the Second Law. Earman and Norton (1998, 1999) argue that, insofar as arguments of this sort are sound, they beg the question by assuming the probabilistic Second Law. They are particularly skeptical of the notion that informational considerations can shed much light on the matter. Indeed, introduction of such notions may seem like a fundamentally ill-conceived endeavour, as many proposed demonizing schemes seem to involve no part that plays the role of an information processor. Moreover, as Zhang and Zhang (1992) have shown, if one is willing to countenance dynamics that does not preserve phase voluume, then an entropy-decreasing device *can* be constructed, and there seems no natural way to construe the operation of Zhang and Zhang's device as involving information acquisition or processing. "[A]nthropomorphising of the Demon is a mistake" (Earman and Norton, 1999, p. 4).

Maxwell's view casts an interesting light on this literature. As we have seen, for Maxwell, the fundamental concepts of thermodynamics are agent-relative; the distinction between heat transfer and work involves a distinction between those degrees of freedom of a system that we have knowledge of and control over, and those that we don't. Whether or not there is an increase in entropy when gases interdiffuse depends on whether the gases are the same or distinct, and this judgment turns on whether we have the means to separate the gases. One could imagine, Maxwell seems to suggest, the discovery of differences to be a never-ending one; no two samples of gas, no matter how much alike they seem, would count as absolutely identical.

There is a tension between the notion of a never-ending discovery of differences to be manipulated, and some of Maxwell's other remarks about molecules. In several places in his writings (see 1871, pp. 310–312; 1873, pp. 440-441), Maxwell emphasizes the remarkable fact that all molecules of the same substance, say, hydrogen, have the same properties, regardless of their sources and past histories We now know that this isn't quite right—Maxwell was unaware of isotopes—but something like it is right. Any two molecules of isotopically identical atomic constituents, in their ground states, are absolutely identical, according to quantum theory. There could, therefore, be no differentially permeable membrane that would distinguish between two samples of gas composed of such molecules. The process of finding of differences must come to an end.

To separate out samples of, say, pure monoisotopic hydrogen gas that had been permitted to interdiffuse, we would, therefore, need the demon's powers of keeping track of all the molecules in the gas. Now, though Poincaré speaks of the demon's "infinitely subtle eye," Maxwell himself emphasized that his demon's capacities are as finite as our own. If a sequence of demons of ever-increasing powers of discernment and manipulation is physically possible, then there could be no absolute definition of entropy and no absolute answer to the question of whether, in a given process, there has been an entropy increase. If, however, it can be shown that any sequence of ever-more-adroit demons must bottom out, then an absolute definition of entropy is not inconceivable; energy has been truly, irreversibly dissipated—entropy has unambiguously increased—when it has become unavailable to maximally adroit demons, where "maximally adroit" means that the demon makes the best possible use, in terms of generating entropy decrease of the target system, of any energy it dissipates in the process of its operations. One can measure the success of a demon in terms of expected entropy decrease generated in the target system per unit entropy increase in the system consisting of the demon and the portion of its environment that it is using to dump its waste heat; the probabilistic version of the Second Law says that this ratio can never exceed unity.

Thus, the attempts to show that there is a limit to the skill that a demon can possess, either because of quantum limitations on information acquisition, or because of the thermodynamics of information processing, can be seen as consistency arguments for standard statistical mechanics. Without such a limit, there can be no absolute answer to the question of how much a system's entropy has increased as it passes from one equilibrium state to another. This makes the introduction of notions associated with information seem less ill-motivated than they might otherwise seem. That is not to say that this is the self-conscious goal of the literature in question, or that it has been successful in achieving this goal. Earman and Norton in their joint articles, and Norton in his follow-ups (Norton, 2005, 2010) make a persuasive case that there is much that is obscure and confused in the literature. Nonetheless, one might still hold out the hope that application of information theory, together with appropriate physical principles, might help us understand *why* (if indeed this is the case) the sequence of ever-more-adroit demons must bottom out in maximally adroit demons that are incapable of violating the probabilistic version of the Second Law.

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