Statistical mechanics and thermodynamics: A Maxwellian view

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A R T I C L E I N F O

A B S T R A C T

One finds, in Maxwell's writings on thermodynamics and statistical physics, a conception of the nature of these subjects that differs in interesting ways from the way they are usually conceived. In particular, though—in agreement with the currently accepted view—Maxwell maintains that the second law of thermodynamics, as originally conceived, cannot be strictly true, the replacement he proposes is different from the version accepted by most physicists today. The modification of the second law accepted by most physicists is a probabilistic one: although statistical fluctuations will result in occasional spontaneous differences in temperature or pressure, there is no way to predictably and reliably harness these to produce large violations of the original version of the second law. Maxwell advocates a version of the second law that is strictly weaker; the validity of even this probabilistic version is of limited scope, limited to situations in which we are dealing with large numbers of molecules *en masse* and have no ability to manipulate individual molecules. Connected with this is his conception of the thermodynamic concepts of heat, work, and entropy; on the Maxwellian view, these are concept that must be relativized to the means we have available for gathering information about and manipulating physical systems. The Maxwellian view is one that deserves serious consideration in discussions of the foundation of statistical mechanics. It has relevance for the project of recovering thermodynamics from statistical mechanics because, in such a project, it matters *which* version of the second law we are trying to recover.

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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, Brush, and Everitt (1995, p. 19).

1. Introduction

The nineteenth-century physicists who developed the kinetic theory of heat and laid the groundwork for the science that we now call statistical mechanics had to wrestle with the implications of their work for thermodynamics. On the kinetic theory, heat is not a substance, but rather is associated with the kinetic energy of molecules. Moreover, on the kinetic theory, the second law of thermodynamics, as originally conceived, cannot be strictly correct, although a suitable successor to it could be. These considerations require a reconceptualizaton of thermodynamics.

One of those who thought deeply about the relations between the theories was James Clerk Maxwell, and the conclusions that he came to about the scope and limitations of the second law of

thermodynamics, and about the nature of the distinction between work and heat, deserve to be better known. For Maxwell, no matter of physical principle precludes the operations of a Maxwell demon; it is only our current, but perhaps temporary, inability to manipulate molecules individually that prevents us from doing what the demon would be able to do. For Maxwell, the distinction between work and heat is not absolute, but relative to the means we have of keeping track of the motion of molecules and of manipulating them. It follows from this that the difference in thermodynamic entropy between two equilibrium states of a system is also means-relative.

In this paper the Maxwellian view of thermodynamics and statistical mechanics will be presented, together with Maxwell's reasons for holding such a view. In the final section the viability of the view will be considered, and it will be argued that, at the very least, no conclusive refutation of the view exists in the literature. I conclude that the view is one that ought to be on the table for serious consideration, in our discussions of the foundations of statistical mechanics.

2. Three second laws of thermodynamics

It has become a commonplace that there are two distinct versions of the second law of thermodynamics. The original deems it impossible that there be a transfer of heat from a cooler body to

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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 the following:

> 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. Considerations of reversibility, which show that anti-thermodynamic behaviour is not ruled out by the laws of mechanics, were instrumental in this for Maxwell, Thomson, and Tait, as they were for Boltzmann (see Brown, Myrvold, & Uffink, 2009; Uffink, 2007, for discussions of Boltzmann's probabilistic turn).

The reversibility argument is spelled out in a letter, dated December 6, 1870, from Maxwell to John William Strutt, Baron Rayleigh; Maxwell follows this with an exposition of what we now call Maxwell's demon,[1] 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 (1871) *Theory of Heat*, 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 an increase of entropy associated, 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 open the possibility that such conditions would, in the normal course of things, be so improbable that they would be 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. 670–671).

The second law of thermodynamics, as originally conceived, must be acknowledged to be false. A plausible successor to it is the probabilistic version. Maxwell, also, thought that a suitably limited version of the second law could be correct. But 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 what 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 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,

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[1] Although Maxwell says that it was William Thomson (who was to become Lord Kelvin) who gave the creatures this name (Knott, 1911, p. 214), Thomson (1874, p. 441) 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.

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 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 it 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.

3. Work, heat, and entropy as means-relative concepts

Maxwell's conception of the status of the second law ties in with his conception of the status and purpose of the science of thermodynamics.

Central to thermodynamics is a distinction between two ways 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 very 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.[2]

To see that this hangs on a distinction between heat and work, note that it becomes false if we do not specify that the energy is transferred as heat. It is not true that *no* energy can 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 statement 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 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; the resulting motions cannot be tracked. This limits our ability to recover the energy as work.

Put this way, the distinction seems to rest on anthropocentric considerations, or, better, on consideration of the means we have available to us for keeping track of and manipulating molecules. We shall call considerations that turn on the means available to an agent for gathering information about a system or for manipulating it *means-relative*; these are matters that can vary between agents, but it would be misleading to call them subjective, as we are considering limitations on the physical means that are at the agents' disposal. On Maxwell's view, the distinction between work and heat is means-relative.

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).

That there is some energy that, for us, counts as dissipated energy has to do, according to Maxwell, with the large number and small size of the molecules that make up a macroscopic body.

The second law relates to that kind of communication of energy which we call the transfer of heat as distinguished from another kind of communication of energy which we call work. According to the molecular theory the only difference between these two kinds of communication of energy is that the motions and displacements which are concerned in the communication of heat are those of molecules, and are so numerous, so small individually, and so irregular in their distribution, that they quite escape all our methods of observation; whereas when the motions and displacements are those of visible bodies consisting of great numbers of

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

molecules moving all together, the communication of energy is called work (Maxwell, 1878b, p. 279; Niven, 1965, p. 669).

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

$$\Delta S = \int \frac{\mathrm{d}Q}{T},\tag{1}$$

where the integral is taken over any quasistatic process joining the two states, and $\mathrm{d}Q$ is the increment in heat absorbed from the system's environment. Thus, on Maxwell's view, the very concepts required to state the second law of thermodynamics are means-relative.

One argument that Maxwell gives for the conclusion that the distinction between available and dissipated energy is means-relative is based 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, containing samples of gas at the same temperature and pressure. The partition is removed, and the gases from the two sub-compartments 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 entropy increase associated with free expansion of the two gases from their initial to their final volumes. He then comments on this distinction:

> 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).

On Maxwell's view, whether or not the interdiffusion of two gases involves an increase of the entropy of the system is not a feature of the physical change alone, but has to do with the abilities of the agent. An agent who saw no way to separate two gases would not regard their interdiffusion as a lost opportunity to do work. Any distinction between the gases that is irrelevant to their capacity to do work is irrelevant to their thermodynamic state, so such an agent would regard the beginning and end states as the same thermodynamic state, and hence judge no increase in entropy.

If we are in possession of a means to separate the gases—say, a membrane permeable to one gas and not to the other[3]—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. In such a process, the gas has increased its entropy, while decreasing the entropy of the reservoir.

Thus, an agent with superior means of manipulation would be able to perform what looked to another agent like a violation of the second law of thermodynamics. Suppose that Bob regards the samples of gas in two compartments separated by a partition as identical. Alice, on the other hand, knows a difference between them and is in possession of membranes, each permeable to one gas but not the other. She can isothermally expand each gas, raising a weight as she does so, while extracting heat from a reservoir. On Bob's parsing of things, the beginning and end states

of the gas are counted as the same, and it looks as if Alice has used the gas as a heat engine with perfect efficiency. Alice, of course, does not regard the process as a violation of the second law, as she does not regard the initial and final states of the gas as the same thermodynamic state.

If we were to discover a hitherto unsuspected difference between two types of molecules, one that permitted us to perform manipulations that could not otherwise have been done, we would not say that the second law of thermodynamics, in any version, had been violated; we would revise our estimates of the entropy of some systems involving these molecules. One can imagine the process of refining our ability to manipulate molecules to go on without limit, with consequent revisions in our estimate of entropy of systems. In such a case, there would be no absolute answer to the question of what the entropy difference of two equilibrium states of a system is.

So far we have been discussing differing means of manipulating molecules in bulk. These yield differing judgments concerning the value of the entropy change of a system as it goes from one equilibrium state to another. If, however, there were an agent capable of manipulating individual molecules, then, according to Maxwell, the distinction between heat and work would break down. "[W]e 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" (Maxwell, 1878b, p. 279; Niven, 1965, p. 669). As long as we are dealing with molecules in bulk, we can distinguish between work, consisting of change of macroscopic variables, and heat, energy distributed in a disorderly manner among many molecules. But from the perspective of a Maxwell demon, there would be no distinction between heat and work, and the very concepts needed to formulate the second law would break down, and thus the second law would be inapplicable, because the very concepts needed to formulate it would fail to apply. Its machinations would, however, look like a violation of the second law, as formulated using any distinction between heat and work.

4. Significance for statistical mechanics

There is more than historical interest in all of this. If it is a goal of statistical mechanics to recover the laws of thermodynamics, then it matters *which* version of the second law is to be recovered. If the very concepts of thermodynamics are means-relative, then it will be necessary to invoke means-relative considerations in the task of finding statistical–mechanical analogues of thermodynamic quantities. If the scope of what is to be recovered is limited to situations in which large numbers of molecules are being treated in bulk, then we can expect to invoke some version of the law of large numbers.

What one would expect to be able to derive from statistical mechanics, on Maxwell's view, might be something akin to the following. The object of our study will be a system with a large number of degrees of freedom. Our knowledge of the state of the system is limited to a small number of quantities, which, typically, will involve sums of a large number of molecular quantities and so, on a probability distribution on which the states of the molecules are independent (as will be the case for equilibrium distributions) these will have small dispersion, and so having precise knowledge of their values will be compatible with considerable ignorance of the microstate of our system. It is in terms of these quantities that we define the thermodynamic state. We also distinguish between types of interaction of the system with its environment. In many

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[3] 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).

circumstances, the forces to which a system is subject can be partitioned into terms dependent on a small number of parameters that we can manipulate (think of the positions of the walls of the container), plus terms that are effectively random (interaction with a heat bath). Energy imparted to (or taken from) the system via changes of the controllable external parameters is to be counted as work; all other energy transfer between the system and the environment, as heat. Assume that there is a reliable relation between the values of the known variables and the controllable parameters (equation of state). On the Maxwellian view, the second law should say that, given such a distinction between manipulable and uncontrollable parameters, and between the known parameters, used to define the thermodynamic state, the unknown, there can be no process that predictably and reliably has the effect of converting heat energy entirely into work with no net change in the thermodynamic states of the systems involved.

This is considerably weaker than the second law of thermodynamics as usually construed. In particular, it says nothing at all about whether it might become possible to convert quantities that are at present beyond our cognizance into knowable quantities, and parameters that we do not currently count as manipulable into manipulable ones. As a consequence, this version places no absolute limits on what can and cannot be done.

A view similar to Maxwell's has, in more recent years, been championed by Jaynes (1965, p. 398, 1989, p. 86), who expresses his view as "Entropy is an anthropomorphic concept."[4]

> 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 (1992, p. 10) proposes his own modification of the second law:

> 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 $\{X_1, \ldots, X_n\}$ that we have chosen to define our macrostate.

This is much in the spirit of a Maxwellian view of thermodynamics.

5. On the meaning of "statistical"

For Maxwell, the truth of the second law is "a statistical, not mathematical, truth" (Maxwell, 1878b, p. 279; Niven, 1965, p. 670). In a letter to Tait he wrote that the chief end of a Maxwell demon is to "show that the second 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 (1998, p. 436) write

Maxwell conceived of the Demon as a helpful spirit, assisting us to recognize 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.

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.[5]

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).

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[4] Jaynes attributes this phrase to Wigner. He arrives at this position via a close reading of Gibbs (1875), and the view, as in Maxwell, is motivated by consideration of the entropy of mixing.

[5] 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.

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, Maxwell (1873) 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 groups. 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, pp. 373–374).

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, on Maxwell's view, it is only insofar as we do so that the second law is applicable.

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, these fluctuations 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 (1976, p. 589), 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.

Maxwell's interpretation of the second law, Brush notes, "is statistical rather than stochastic" (Brush, 1976, p. 593). Maroney (2009), 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.

6. Exorcising the demon?

Most contemporary physicists believe in something considerably stronger than this Maxwellian law. We should ask whether we have a good reason to believe the stronger version; and this is the question of whether we have reason to believe that there could be no device that played the role of Maxwell's demon, predictably and reliably converting what we (presently) regard as heat entirely into useful work. A reply that the second law is a well-confirmed inductive generalization would not be persuasive. On the Maxwellian view, the second law is valid in situations in which there is no manipulation of individual molecules, and these are the circumstances of the observations that form our basis for induction. That something has never been observed is not a good argument that it is not technologically feasible; we are familiar with phenomena that can be produced artificially, but which occur rarely, if at all, in nature. A convincing argument would have to derive the probabilistic second law from some principle for which we can provide independent grounds.

There is an extensive literature that attempts to do just this (see Leff & 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, according to which erasure of a record that represents n bits of information inevitably results in a minimum average entropy increase of $nk \ln 2$, where k is Boltzmann's constant.

Earman and Norton (1998, 1999; see also Norton, 2005) 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 volume, 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 & Norton, 1999, p. 4).

> even if the operation of the Demon involves what deserves to be called an information processor of computer—a dubious assumption in some cases—the ultimate explanation for the possibility or impossibility of various operations must be traced to fundamental physical laws, laws which are stated without the mention or use of information concepts. One thus suspects that at best what information considerations can offer us is a handy heuristic (Earman & Norton, 1999, p. 24).

"At best"; the bulk of Earman and Norton's discussion suggests that invocation of informational considerations more commonly serves as a smoke-screen to hide the fact that the second law is being assumed as a premise, only to be rederived as a conclusion.

The Maxwellian view casts an interesting light on this literature. If the very concepts of thermodynamics are means-relative, and we cannot even state the second law of thermodynamics without invoking a means-relative distinction between heat transfer and doing work, then anthropomorphising the demon no longer seems like a mistake. On Maxwell's view, dissipation of energy simply *is* the transfer of energy from degrees of freedom we keep track of to ones that we do not. Landauer's principle, on this view, looks, not like an unprovable and dubious assumption, but a tautology.

If Landauer's principle is a tautology, though, it will be of no avail in determining what is and is not physically possible. If all we will obtain from statistical mechanics is an agent-relative version of the second law, this will be of no use in determining which manipulations might be feasible, and which are not. So, even if we accept that information-theoretic conceptions deserve a central place in thermodynamics and statistical mechanics, they are out of place in determining what can and can not be done physically. For this, we need to look to physics itself, and, as Earman and Norton have argued, no argument of the requisite sort has been produced.

In light of all this, the Maxwellian view, whether it is correct or not, is the one that deserves to be on the table in discussions of the foundations of statistical mechanics. We should take seriously the idea that thermodynamic concepts are inherently means-relative. If we are dealing with large numbers of molecule in bulk, there will usually be a notion of dissipation of energy that is sufficiently clear that, in practice, we can employ thermodynamic concepts in such a way that ambiguity is kept small enough that it does not become a nuisance, but, if the Maxwellian view is correct, it would be a mistake to search for absolute physical meaning of these concepts.

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