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The nineteenth century conflict between mechanism and irreversibility

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ABSTRACT

The reversibility problem (better known as the reversibility objection) is usually taken to be an internal problem in the kinetic theory of gases, namely the problem of how to account for the second law of thermodynamics within this theory. Historically, it is seen as an objection that was raised against Boltzmann's kinetic theory of gases, which led Boltzmann to a statistical approach to the kinetic theory, culminating in the development of statistical mechanics. In this paper, I show that in the late nineteenth century, the reversibility problem had a much broader significance—it was widely discussed and certainly not only as an objection to Boltzmann's kinetic theory of gases. In this period, there was a conflict between mechanism and irreversibility in physics which was tied up with central issues in philosophy of science such as materialism, empiricism and the need for mechanistic foundations of physical theories, as well as with concerns about the heat death of the universe. I discuss how this conflict was handled by the major physicists of the period, such as Maxwell, Kelvin, Duhem, Poincaré, Mach and Planck, as well as by a number of lesser-known authors.

1. Introduction

The reversibility problem—which has become known as the reversibility *objection* (or *Umkehreinwand*)—is well known in the literature as an objection that was raised against Boltzmann's kinetic theory of gases, an objection with which Boltzmann wrestled for many years.[1] It is usually presented along with the recurrence objection (or *Wiederkehreinwand*) as physical theorems which show that, within the kinetic theory of gases, there is a problem with accounting for the second law of thermodynamics. However, when the reversibility problem first appeared, in the last decades of the nineteenth century, it was the subject of a much broader discussion. For that reason I will speak of the reversibility *problem* rather than the reversibility objection.

The problem lies in the difficulty with giving a mechanical account of irreversible processes. The laws of mechanics are reversible, which means that if you exactly reverse the velocities of all particles in a closed mechanical system, all processes will subsequently run backwards. In a mechanical theory such as the kinetic theory of gases, the reversal of each process is thus a theoretical possibility. There is therefore a conflict between mechanical accounts of nature and the irreversibility that we experience in many daily phenomena and which is reflected in the second law of thermodynamics. This conflict was a much debated issue in late-nineteenth-century physics because it was connected with the most pressing debates of that time: the debate over the need for mechanical foundations in physics versus empirical approaches; materialism; the question whether the laws of nature should be regarded as strictly and universally valid or could also have statistical validity; and the concerns about the heat death of the universe which the second law of thermodynamics seemed to imply. In this paper I show how the reversibility problem served as an argument in each of these debates. When discussing this problem, authors were confronted with conflicting values in physics, such as empiricism versus the need for mechanical foundations, and therefore studying the way in which different authors dealt with the issue of reversibility provides an interesting opportunity to trace developments in the philosophy of physics.

In the first two sections of this paper, the main concepts which play a role in the reversibility problem are clarified, namely irreversibility and mechanism. The rest of the paper is a roughly chronological study of the treatments of the reversibility problem in the second half of the nineteenth century. It is intended to be more or

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[1] See for example Kuhn (1978, p. 46ff), Torretti (2007, p. 745ff), Uffink (2007, p. 929ff).

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less exhaustive, involving the work of many of the leading physicists of the period, including Maxwell, Planck, Mach, Poincaré and Duhem, as well as lesser-known scientists whose work on the reversibility problem has not previously been studied.[2] By including not only well-known physicists in the story but also relatively unknown authors, I intend to give a view of the full dimensions of the debate. In this way I show that the reversibility problem was much more than an internal problem within the kinetic theory of gases.

2. Irreversibility and the second law of thermodynamics

Irreversible processes in physics are those processes which are not physically possible to reverse, or for which a reversal is not allowed by the laws of nature. Here, for any process P which takes a system from an initial state s_1 to a final state s_2, the reverse process is that which takes the system from s_2 to s_1.[3] Examples of processes thought to be irreversible are the melting of an ice cube in a closed system, a body losing speed through friction, and processes of decay and ageing.

During the second half of the nineteenth century, the term "irreversibility" was introduced in physics mainly in the context of the second law of thermodynamics. But the exact relation between irreversibility and the second law of thermodynamics was not always clear, mainly because during the period, it was never entirely clear what exactly the second law of thermodynamics was. The law became established in the 1850s, soon after the first law of thermodynamics (the law of conservation of energy). Although the importance of the second law as a law of nature was soon widely acknowledged, physicists did sometimes remark that it was less well established and received less recognition than the first law of thermodynamics, because it was more complicated and had less clear foundations.[4] The fact that there were actually many different versions of the second law of thermodynamics was both a factor in and a consequence of this confusion. The main versions of the second law that were used at the time are the following:

(1) The statement that there is an entropy function in thermodynamics which can never decrease (that is, in adiabatically isolated processes). This implies that all processes in which entropy increases are irreversible.
(2) The principles of Thomson (the later Lord Kelvin) and Clausius (cited in Uffink (2001, p. 327)):
    - [Thomson] 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.
    - [Clausius] It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

    These principles are intended to apply to heat engines working in a cycle. They are empirical principles based on experiences of the behavior of heat: heat always tends to flow from hot bodies to cold bodies, and it takes energy to cool an object below the temperature of its surroundings. These principles, too, forbid the reversal of certain processes. For example, a process in which heat is transferred from a higher temperature to a lower temperature is perfectly possible, but its reversal is not (that is, as long as it is a cyclic process which has the transfer of heat as its only result).
(3) The statement that mechanical energy can be completely converted into heat, but heat cannot be completely converted into mechanical energy. Thus whenever mechanical energy is converted into heat, for example through friction, there is a decrease of the amount of energy that can be converted into mechanical energy: a decrease in "available" energy, also called "dissipation" or "degradation" of energy. This version of the second law was often used by Thomson.[5] It clearly involves irreversibility.
(4) The statement that there is a tendency toward thermal equilibrium: in isolated systems, differences in heat and temperature always tend to disappear. This statement also clearly involves irreversibility, but it is not clear whether it can be regarded as a formulation of the second law of thermodynamics. It can partly be traced back to Fourier's theory of heat conduction from 1822. Brown and Uffink (2001) have called this principle the "minus first law" of thermodynamics, and argue that it is actually through this principle that time asymmetry enters thermodynamics. This would mean that not all irreversibility in nature is connected to the second law of thermodynamics.
(5) The statement that there is an entropy function S such that $d'Q/T = dS$, with $d'Q$ an inexact differential of the heat Q that a system exchanges with a reservoir, and T its temperature. This version of the second law is not connected to irreversibility; the validity of this equation is even limited to processes which are "reversible" in Clausius' sense, which is close to quasi-static (Uffink, 2001, p. 337).

The above versions of the second law are closely related but not exactly equivalent; for the relations between them, see Uffink (2001). Except for (5), all of these statements involve irreversible processes. But although, in the period that I discuss, irreversibility in physics was mainly discussed in the context of the second law, it was not clear whether all irreversible processes were connected to it. In 1879, Max Planck argued that the second law was the unique law that governed all irreversible processes and was therefore the key to understanding irreversibility in nature. Specifically, he argued that all irreversible processes involved an increase of entropy (Planck, 1879). But this view was by no means commonly accepted at the time.

3. Mechanism and the reversibility of mechanical processes

With "mechanism" I mean the attempt to reduce all physical theories to mechanistic theories. By "mechanistic theory" I mean a theory in which all entities are defined in terms of matter, motion, and central forces (forces depending only on distance). Mechanistic theories are often, but not necessarily, atomistic. Alternatively, we might think of a mechanistic theory as a theory which explains natural phenomena in terms of springs, wheels, pulleys, etc., in

[2] A notable omission is Gibbs, who, despite the fact that he made important contributions to both thermodynamics and statistical mechanics, does not seem to have directly discussed the problem of reversibility of mechanical motion versus irreversibility in thermodynamics. Gibbs did point out a problem with the foundations of the second law within the kinetic theory of gases, namely the diffusion paradox that is named after him, and concluded: "In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability". But this has little to do with the reversibility problem otherwise. See Gibbs (1876–1878, p. 167).

[3] In treatises of thermodynamics, the term 'reversible' can also be used to denote a slow and gentle process, during which the system remains close to equilibrium (also called a *quasi-static* process); a process is then 'irreversible' if this does not hold. Note that this definition is not fully equivalent with the above sense of irreversibility. For a thorough treatment of the different notions of irreversibility in physics, see Uffink (2001, p. 315ff).

[4] See for example Loschmidt (1869, p. 395), Wald (1889, p. 2).

[5] He introduced this principle in his 1852 article titled "On a universal tendency in nature to the dissipation of mechanical energy" (Thomson, 1852).

order to show the "mechanism" behind the phenomenon. However, such a theory does not always need to be mechanistic in the strict sense defined above, and in particular, actual mechanisms usually involve a certain amount of friction.

It is an ancient ideal in physics to give mechanical explanations of all phenomena: physicists have often felt that one can only truly understand something after reducing it to understandable, mechanical terms. In the nineteenth century mechanism played an important role in physics, so for example when electromagnetism was developed, physicists like Maxwell, William Thomson and J. J. Thomson attempted to give it a mechanical foundation. According to the latter, the belief in the possibility of mechanical explanation of natural phenomena was "the axiom on which all Modern Physics is founded" (Thomson, 1888, p. 1). Also the attempt to reduce thermodynamics to mechanics was an important project in nineteenth century physics. Thermodynamics itself was evidently not mechanistic, since it employed entities that were not reduced to mechanical entities, such as heat. It was based on empirical principles, for example that heat always tends to flow from hot to cold. To reduce thermodynamics to a mechanistic theory, Clausius, Maxwell, Boltzmann and others developed the kinetic theory of gases, which described the properties of gases in terms of the motion of its atoms or molecules.

A property of such a mechanistic theory is that its laws are time symmetric; therefore, strictly speaking, it does not allow for irreversible processes. Take a mechanical system, and a process which takes the system from its initial state s_1 to a state s_2 within a certain interval of time. Now take the state s_2 and instantaneously reverse all velocities to obtain the reversed state $R(s_2)$. Then subsequently, a reversed process takes place which takes the system from state $R(s_2)$ to state $R(s_1)$. If the original process showed an increase in entropy, the reverse process shows a decrease in entropy. This reversal of all velocities at an instant may not actually be practicable, but nevertheless the thought experiment shows that for each process $P: s_1 \rightarrow s_2$ that can occur within a certain mechanical system, initial conditions can be found which lead to a reversed process P_R: $R(s_2) \rightarrow R(s_1)$: thus the reversed process is always *physically possible*, that is, it is allowed by the laws of nature.

In practice, macroscopic motion always involves a certain amount of friction, which causes it to be irreversible. However, mechanistic theories do not allow for friction on the fundamental level. The kinetic theory of heat made it possible to explain friction as the transfer of kinetic energy from the moving body to small particles in its surroundings, whose motion constitutes heat. It follows from this explanation of friction that if the velocity of all particles, including the particles in the surrounding environment, is exactly reversed then even a process involving friction becomes reversed.

4. Reversibility and materialism

An early appearance of the principle of reversibility of mechanical motion can be found in the correspondence between James Clerk Maxwell and William Thomson (the later Lord Kelvin). In a letter from 1857, in which Maxwell discussed the properties of motion in a perfect fluid (one without viscosity or fluid friction), he remarked:

> If you pour a perfect fluid from any height into a perfectly hard or perfectly elastic basin its motion will break up into eddies innumerable forming on the whole one large eddy in the basin depending on the total moments of momenta for the mass.
>
> If after a given time say 1 h you reverse every motion of every particle, the eddies will all unwind themselves till at the end of another hour there is a great commotion in the basin, and the water flies up in a fountain to the vessel above. But all this depends on the *exact* reversal for the motions are *unstable* and an approximate reversal would only produce *a new set of eddies multiplying by division* (Maxwell, 1857).

Although Maxwell emphasized that the reversal of the process of pouring a perfect fluid is virtually impossible in practice (he added: "I do not see why the unstable motion of a perfect fluid should not produce eddies which can never be gathered up again except by miracle"), he did recognize that the process is reversible in principle. However, this did not mean that he thought that the reversal of every process was possible. In a letter that was published in the *Saturday Review* (Maxwell, 1868), he attributed such a view to unnamed materialists. A materialist, believing that everything can be reduced to matter and motion, must accept the idea that every process can also occur in reverse:

> …one thing in which the materialist (fortified with dynamical knowledge) believes is that if every motion great & small were accurately reversed, and the world left to itself again, everything would happen backwards: the fresh water would collect out of the sea and run up the rivers and finally fly up to the clouds in drops which would extract heat from the air and evaporate and afterwards in condensing would shoot out rays of light to the sun and so on. Of course all living things would regrede from the grave to the cradle and we should have a memory of the future but not of the past (Maxwell, 1868).

Maxwell thus argued that materialism leads to consequences which are evidently in conflict with common sense. He was committed to mechanism and was one of the main physicists involved in the attempt to reduce all physical phenomena to mechanics, and he therefore had to acknowledge that all purely physical processes are reversible, although their actual reversal may have a probability close to zero. But Maxwell was no materialist; a deeply religious man, he thought that the ultimate nature of things was fundamentally unknowable, and he was opposed to the scientific materialism of John Tyndall and others (Harman, 1998, pp. 197–208). He did not think that processes involving life could be fully explained mechanically; in an essay from 1873 he argued that the laws of physics could allow for the possibility of a soul to act in living beings, thus introducing indeterminism (Maxwell, 1873, p. 817ff). If a living system could not fully be described in a mechanistic, deterministic manner, it seems likely that it would not be subject to reversibility. It is likely that Maxwell therefore rejected the conclusion that "all living things would regrede from the grave to the cradle", although he did not make this line of thought explicit.

The argument for the non-reversibility of processes involving life can be found in explicit form in an article about the reversibility problem by Maxwell's friend Thomson, published in 1874. Thomson argues that if at a certain moment the velocities of all the particles in the universe were exactly reversed, the result would be a complete reversal of "the course of nature":

> The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water; the thermal motions would reconcentrate their energy, and throw the mass up the fall in drops re-forming into a close column of ascending water. Heat which had been generated by the friction of solids and dissipated by conduction, and radiation with absorption, would come again to the place of contact, and throw the moving body back against the force to which it had previously yielded. Boulders would recover from the mud the materials required to rebuild them into their previous jagged forms, and they would become reunited to the mountain peak from which they

> had formerly broken away. And *if also the materialistic hypothesis of life were true*, living creatures would grow backwards, with conscious knowledge of the future, but no memory of the past, and would become again unborn. (Thomson, 1874, pp. 351–352; Brush, 2003) [my italics].

However, Thomson did not think that the materialistic hypothesis of life was true. He continued: "the real phenomena of life infinitely transcend human science; and speculation regarding consequences of their imagined reversal is utterly unprofitable" (Thomson, 1874, p. 352; Brush, 2003). As he wrote many years later:

> The considerations of ideal reversibility, by which Carnot was led to his theory, and the true reversibility of every motion in pure dynamics have no place in the world of life. Even to think of it (and on the merely dynamical hypothesis of life we can think of it as understandingly as of the origination of life and evolution of living beings without creative power), we must imagine men, with conscious knowledge of the future but with no memory of the past, growing backward and becoming again unborn; and plants growing downwards into the seeds from which they sprang (Thomson, 1892, p. 464).

A similar argument can be found in the writings of the Belgian Jesuit Ignace Carbonnelle, mathematician and philosopher, who argued against materialism from a Catholic point of view. Like Maxwell and Thomson, he argued that the reversal of purely material processes was theoretically possible, though very improbable. But it would be absurd to think that "les phénomènes de l'ordre intellectuel et moral"[6] are reversible, and thus these phenomena cannot be purely material (Carbonnelle, 1881, p. 336).

In an 1875 article about the reversibility problem by Philippe Breton, a little-known engineer from Grenoble with an interest in philosophy, we also find the argument against materialism (Breton, 1875). In this article, Breton points out that the fact that processes generally take place in a definite direction and the fact that causes always precede their effects are not reflected in the equations of mechanics, which are time symmetric. Therefore, according to the laws of mechanics, the original and the reversed processes are equally possible. In the case of the study of comets, this leads to the valuable insight that comets which are caught in the solar system are not necessarily caught forever but might move away after a certain time. But Breton finds other examples more disturbing: according to the "materialistic world view", the process of a stone breaking to pieces must also be reversible, as well as the process of ripening and rotting of fruit, the process of ageing… Breton writes about reversed sensations, reversed memories, reversed will and morality, and even about reversed Darwinism—an important theory for the true materialist, according to which the environment adapts itself to the changing animal. Furthermore, he argues that when the possibility of the reversal of all processes is taken into account, it is no longer possible to distinguish causes from effects.

Breton's conclusion is clear: "Il est donc évident que la mécanique n'est pas la science universelle".[7] To avoid absurdity one has to conclude that not everything is reducible to matter and motion. The laws of mechanics were derived from a limited set of phenomena and are thus only applicable within a limited domain. Breton also argues that mechanics is ultimately based on common sense, so if it leads to results that are in conflict with common sense, then one should suspect there is something wrong with its foundations instead of uncritically accepting the results.

According to Maxwell, Thomson, Carbonnelle and Breton, there is thus a limit on which processes should be thought to be reversible. The physicist may have to admit that it is theoretically possible that processes such as the falling of an object or the melting of ice can also occur in reverse, but presumably, for these authors the thought of people growing younger is simply absurd and should not be accepted. Their motivation for arguing that materialism ultimately leads to such absurd consequences was to make materialism itself seem absurd.

5. Reversibility and statistical laws of nature

Both Thomson and Maxwell did accept the reversibility (at least in theory) of those processes which did not involve life or the mind. The idea that appears from Maxwell's writings is that there are physical processes which may be called irreversible, but only in the sense that the reversed process is exceedingly improbable, a fact that depends on contingent properties of the world. Theoretically, each physical process is reversible. This reversibility entails that violations of the second law of thermodynamics (or at least most versions of it) are theoretically possible, although the probability that the second law is violated on an observable scale is extremely small (see Maxwell, 1878, p. 285ff). For Maxwell, the reversibility problem showed that the second law was a *statistical* law of nature (see Porter (1986, p. 111ff), about the role of the statistical method in Maxwell's thought).

In addition to the reversibility thought experiment, Maxwell came up with a second thought experiment which showed that violations of the second law of thermodynamics were theoretically possible, which is now known as "Maxwell's demon". Maxwell's demon is a small being that can observe and manipulate individual atoms. By moving a frictionless slide to open and close a hole in a wall between two vessels, this being can let slowly moving atoms pass through only to one side and quickly moving atoms only to the other side. In this way, he can make heat flow from cold to hot without performing work; this means a violation of the second law of thermodynamics. Maxwell concluded that the validity of the second law depends on the assumption that we as human beings cannot perform this operation: the particles whose motion is experienced by us as heat just happen to be too small for us to observe and manipulate (Maxwell, 1871 1970, pp. 153–154). In a letter to John William Strutt (the later Third Baron Rayleigh), Maxwell explained both the reversibility problem and the demon, and concluded:

> *Moral*. The 2nd law of thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea you cannot get the same tumblerful of water out again (Maxwell, 1870b).

Despite the significance of the second law in Maxwell's thought, he did not seem to regret the fact that, according to the kinetic theory of gases, the second law was not universally valid. This has much to do with his conviction that, although the truth of the second law was "not of the same order as that of the first law", it was still a reliable statement, just as the statement that "if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again" was reliable. The relevant point was not whether exceptions to the second law are theoretically possible, but whether it holds in practice in the world as we experience it, and one may say that it does.

Thomson also had no difficulty in allowing that the second law could theoretically be violated. He did not even perceive a tension between mechanism and irreversibility: in his 1874 article he wrote that "a very elementary consideration of [the reversibility of mechanical motion] leads to the full explanation of the theory of dissipation of energy" (Thomson, 1874, p. 352). Apparently, according to Thomson, the reversibility problem not only did not

[6] "the phenomena of the intellectual and moral order".

[7] "It is thus evident that mechanics is not the universal science".

threaten the principle of energy dissipation (version (3) of the second law) but even clarified it. As an example he mentioned a process of temperature equalization in a body composed of freely moving atoms, and argued that a spontaneous reversal of this process is a statistical possibility, but that one can explain why such a process of disequalization is never observed in practice by calculating how extremely small its probability is.

The reversibility problem, together with Maxwell's demon, played a central role in the development of the idea of statistical laws of nature, and the change of the second law of thermodynamics from an absolute to a statistical law of nature was a crucial step in the development of statistical mechanics.

6. Reversibility and the heat death of the universe

It is somewhat surprising that Maxwell and Thomson had no difficulty giving up on the absolute validity of the second law, given that both attached great importance to the law. According to Thomson, who was one of the physicists who developed the second law, the law predicts that our world is inevitably evolving towards a final state, in which it will be "unfit for the habitation of man as presently constituted" (Thomson, 1852). This final state has come to be known as the heat death, a state in which all energy is converted into heat, uniformly distributed through space, and all motion has ceased. But not only did the second law predict a heat death, it also pointed at an origin in time of the universe, as Kragh (2008) has shown. Temperature differences cannot have been diminishing forever, mechanical energy cannot have been irrecoverably converted into heat forever. Thus, there must have been a temporal origin for these processes, which could be connected with divine creation; Maxwell and Thomson both connected the second law (or the law of dissipation of energy) with such a temporal origin (Maxwell, 1870a, p. 226; Thomson, 1852). Smith and Wise (1989, p. 330ff) have argued that the idea of directionality in nature deeply influenced Thomson's work.

However, not everyone was pleased with these cosmic implications of the second law. The German chemist and physicist Joseph Loschmidt was greatly troubled by the prospect of the heat death of the universe, and these concerns led him to use the reversibility problem to argue that the second law had to be rejected altogether, or at least the principles of Thomson and Clausius (version (2) of the second law) and the principle of dissipation of energy (version (3) of the second law).

Loschmidt was a materialist (Loschmidt, 1867, p. 81) and an active proponent of molecular science, famous for his estimation of the size of molecules. He believed that the success of the kinetic theory of gases greatly supported atomism (Loschmidt, 1866, p. 646). His enthusiasm for the second law of thermodynamics seems to have been more limited from the start. In a popular lecture in 1867, he mentioned Clausius' principle (version (2) of the second law) and the fact that a consequence of this principle was the heat death of the universe. He concluded:

> Wir haben dann vollkommene Ruhe in allen Welten, die ewige Ruhe des allgemeinen Todes.
>
> Mann hat die grössten Anstrengungen gemacht, einen Ausweg zu finden, diesen wenig erbaulichen Folgerungen zu entgehen, bisher vergeblich, und es ist wenig Aussicht vorhanden, dass es noch gelingen werde.[8] (Loschmidt, 1867, p. 66)

Despite the fact that Loschmidt's hopes for disproving the heat death of the universe were initially low, he set out to examine the foundations of the second law. In 1869, he argued that this law was still lacking a solid foundation and a clear exposition of its meaning, though "weitgreifenden Deductionen"[9] were generally drawn from it (Loschmidt, 1869, p. 395). It appears that Loschmidt thought that basing a law of nature on an empirical principle was not rigorous enough. He argued that one cannot be sure that Clausius' principle that heat can never flow from a cold to a hot body without compensation is universally valid, even though we never observe a violation of it: there may be circumstances which prevent us from observing the transition of heat from a cold to a hot body. Loschmidt continues:

> Es ist daher jedenfalls gerathen zuzusehen, ob nicht im Wesen der molecularen Wärmebewegung selber Gründe aufzufinden seien, welche für oder gegen die Möglichkeit eines solchen Überganges sprechen (Loschmidt, 1869, p. 399).[10]

His subsequent considerations of molecular motion led him to a thought experiment similar to that of Maxwell's demon. Take a space with a large amount of gas molecules, in which the average velocity of the molecules remains constant but the individual velocities vary in time and amongst each other. Take a second, smaller space separated from the first by a wall with a hole in it. If the initial condition of the gas is known at the molecular level, then, since the system is deterministic, it is possible to calculate at which moments and with what velocities the molecules will hit the wall at a given place. Thus one can calculate in advance at which moments to open or close the hole in the wall in order to let through only molecules with velocities above the average. In this way heat can be made to flow from the large space to the smaller one, also when this entails a heat flow from a cold to a hot space. It is even possible to make the density of the gas in the smaller space rise above that in the larger space.

No demon-like being is employed here, but to perform this experiment one does need to be able to observe the behavior of individual molecules (in order to know the initial positions and velocities of all molecules) and to be able to open and close a hole in the wall quickly enough to let individual molecules through: these are exactly the faculties that Maxwell proposed for his demon. So the only difference between Maxwell's and Loschmidt's thought experiments is that Loschmidt employs the determinism of the system to relieve the door-handler of making his decisions at the moment a molecule approaches. And, most significantly, Loschmidt uses the thought experiment for a different end: he does not use it in order to argue that the second law depends on the assumption that one cannot observe and manipulate individual particles, as Maxwell did, but to argue that it is problematic to give a mechanistic account of the second law. This, however, did not lead him immediately to renounce the second law:

> Nichtsdestoweniger mag auch hier der zweite Hauptsatz seine Giltigkeit behaupten, und es ist vielleicht nur der Beweis, welcher da auf eine andere Weise geführt werden müsste (Loschmidt, 1869, p. 406).[11]

But, in an article from 1876, Loschmidt brought up more problems for the possibility of giving a mechanistic account of the second law. The article dealt with the temperature of a column of gas in a gravitational force field, a problem about which there was a debate at the time: in 1866, Maxwell had derived on the basis of the kinetic theory of gases that the temperature in a column of gas

[8] "We then have complete rest in all worlds, the eternal rest of overall death. The greatest efforts have been made to find a way to escape these not very edifying inferences, so far in vain, and little hope of success remains."

[9] "Far-reaching deductions".

[10] "It is therefore in any case advisable to see if in the nature of molecular thermal motion itself there cannot be found grounds on which one can decide for or against the possibility of such a transition".

[11] "Nevertheless, the second law may keep its validity here as well, and it is possibly only its proof that must be derived in a different way".

subjected to gravity is uniform (Brush, 1976, p. 149), but Loschmidt thought that Maxwell's derivation was incorrect and put forward a (not very convincing) argument to show that the temperature actually decreases with height. He also showed that if this is the case, a system can be devised in which there is a continuous heat flow, which means that the empirical principles of Thomson and Clausius (version (2) of the second law) are violated. This violation does not mean that the second law itself is overturned: version (5) of the second law still holds. But Loschmidt was glad with the result that Thomson's and Clausius empirical principles can be violated:

> Damit wäre auch der terroristische Nimbus des zweiten Hauptsatzes zerstört, welcher ihn als vernichtendes Princip des gesammten Lebens des Universums erscheinen lässt, und zugleich würde die tröstliche Perspective eröffnet, dass das Menschengeschlecht betreffs der Umsetzung von Wärme in Arbeit nicht einzig auf die Intervention der Steinkohle oder der Sonne angewiesen ist, sondern für alle Zeiten einen unerschöpflichen Vorrath verwandelbarer Wärme zur Verfügung haben werde. (Loschmidt, 1876, p. 135).[12]

More support for this claim was given by the reversibility problem. Loschmidt argued that one cannot be sure that a "so-called stationary state" of a gaseous system, when left undisturbed, will last forever. The case he considered was that of a container filled with gas in a homogeneous gravitational field, in which initially one atom is set in motion while all the others are at rest at the bottom of the container. The moving atom disturbs the other atoms until all are in motion in what appears to be a stable state of the gas. Suppose now that the velocities of all atoms are reversed at an instant. At first the gas will appear to remain close to its stationary state, but after a certain time, one single atom will have absorbed all kinetic energy while the other atoms lie still at the bottom.

> Offenbar muss ganz allgemein, in jedem beliebigen System, der gesammte Verlauf der Begebenheiten rückläufig werden, wenn momentan die Geschwindigkeiten aller seiner Elemente umgekehrt werden. (Loschmidt, 1876, p. 139).[13]

Ironically, this remark has become famous as an objection to the kinetic theory of gases, but what Loschmidt intended to show with it was quite the opposite: he intended to support his case against the versions of the second law which involved irreversibility, notably against version (3) of the second law, according to which there is an irreversible transformation of mechanical energy into heat, which leads to energy sources running out and ultimately to heat death. While other physicists based their derivations of the second law on the assumption of the impossibility of endless supplies of transformable heat, Loschmidt used the kinetic theory of gases to undermine this assumption. Motivated by a dislike of the prospect of heat death, he made an extreme choice in the conflict between mechanism and irreversibility.

It is remarkable that both Maxwell's demon and the reversibility problem have appeared seemingly independently in the work of Maxwell and Loschmidt. Porter (1986, p. 211) remarks that Loschmidt invented the reversibility argument independently of Maxwell and Thomson; and while Maxwell first conceived his demon in 1867 and only published about it in his *Theory of Heat* (1871), a similar thought experiment already appeared in the Loschmidt's work in 1869. There are no indications of any contact between them.

7. Reversibility and the nature of time

Not all physicists who discussed the reversibility of mechanical processes recognized a conflict between mechanism and irreversibility. G. Johnstone Stoney was an Irish physicist who had some influence in the kinetic theory of gases and worked on atomic structure; he is best known for introducing the name "electron" and estimating its magnitude in 1874 (Brush, 1976, p. 199). In 1887, he published an article about reversibility of mechanical processes, in which he gave a vivid description of the kind of phenomena that could be observed if the velocities of all the particles in the universe were reversed at an instant, if it were possible to observe these phenomena as it were from a standpoint outside of the system of the universe:

> The bird which was shot to-day by the sportsman, and which is now lying in his kitchen, will, if the reversal of the universe were to take place at this instant, be restored by the keeper to his gamebag, will be carried by him, walking backwards, to the place where the pointer had fetched it in, where he will take it out, and lay it on the ground. Thence the dog will lift it in his mouth, and, trotting backwards, will reach the spot where the bird fell, where, however, it will now rise to the height at which it was shot, from which it will fly away backwards unharmed. Meanwhile, the vapours into which the powder had been dissipated will stream back into the barrel of the fowling-piece, and condense themselves again into gunpowder, while the grains of shot will rush towards the muzzle of the gun, and crowd into its breach (Stoney, 1887, p. 544).

Stoney worked out the thought experiment in order to clarify some physical concepts. The contemplation of reversed processes makes clear that there is a distinction between two types of laws of nature: the truly dynamical laws which remain valid in their original form in the reversed world, for example the law of conservation of energy, and the "quasi-dynamical" laws which do not remain valid, such as the second law of thermodynamics. Furthermore, a distinction can be made between true causes and quasi-causes: true causes are those that instantaneously produce their effect and thus occur simultaneously with it, so that reversal leaves the causal relation intact, while for quasi-causes, cause and effect become reversed through the reversal of processes.

For a further insight, Stoney argues that our thoughts are in fact in the same way susceptible to reversal as any physical event is. Thus a complete reversal of all processes in the universe would reverse the observer's thoughts and memories as well. While watching the reversed universe, one would see nothing special—one would not even notice that all processes occur in the wrong time direction, Stoney argues. Thus, according to him, the direction in which we experience time to pass depends on the direction in which processes take place (Stoney, p. 546). This idea was later expressed by Boltzmann (1897, p. 416), probably independently, and has since then been widely discussed; it has always been attributed to Boltzmann.

According to Stoney, the thought experiment of reversal gives an important insight in the nature of time, namely that time is only an abstraction and does not exist independently of the individual time-relations between thoughts and between events. These time-relations remain unaffected by the reversal, so it is not only impossible to observe a difference between the actual and the reversed world, but in fact, there is no difference.

[12] "Thereby, also the terroristic nimbus of the second law would be destroyed, which makes it appear to be an annihilating principle for all life in the universe; and at the same time the comforting prospect would be opened up that mankind is not only dependent on mineral coal or the sun for transforming heat into work, but rather may have an inexhaustible supply of transformable heat available for all times."

[13] "Clearly, in general the course of events must in any arbitrary system become reversed, if the velocities of all its elements are reversed at an instant."

So Stoney used the thought experiment of reversal to obtain a clarification of the concepts of true dynamical laws and true causes, and to argue that time is only an abstraction. In his discussion of dynamical laws, he mentioned the second law of thermodynamics as a “quasi-dynamical” law, but did not draw any conclusions about its validity. He did not describe the reversibility problem as problematic for either the second law or the kinetic theory of gases; instead he used it to develop some interesting new ideas in physics.

8. Attempts at a mechanical derivation of the second law

The reversibility problem showed that, within the kinetic theory of gases, the reversal of each process is possible and thus the second law can theoretically be violated. Maxwell and Thomson had drawn the conclusion that the second law could only have statistical validity; Loschmidt argued that it should be rejected altogether. In any case, these considerations seemed to make clear that it was not possible to give a mechanical derivation of the second law. Yet, attempts in this direction were made during the period. In this section, I give a very brief discussion of the attempts to derive the second law within the kinetic theory of gases. This is a topic that has already been well described in the literature; for a fuller treatment, see Klein (1973), Kuhn (1978), Cercignani (1998), and Uffink (2007).

There had been attempts at giving a mechanical derivation of the second law of thermodynamics since the 1860s. Some of the earliest attempts, by Boltzmann, Clausius and Szily, concentrated on version (5) of the second law, which did not involve irreversibility, and for which the reversibility problem thus posed no problem (see Klein, 1972; Bierhalter, 1992). In 1872, Boltzmann made a first attempt to give a mechanical derivation of irreversible processes in thermodynamics (Boltzmann, 1872). He derived an expression which he thought to be analogous to the law of increase of entropy (version (1) of the second law), namely that there is a function, later to be named H, for which

$$\frac{dH(f_t)}{dt} \leq 0$$

That is, H may decrease but cannot increase in time. This inequality becomes an equality if and only if an equilibrium distribution is reached. By identifying H with negative entropy, it appears that when a system approaches equilibrium, this approach is accompanied by an increase of entropy, and that this is an irreversible process.

Boltzmann believed he had given a rigorous derivation of his H-theorem; the question remains whether this derivation was thoroughly mechanical. One reason we may doubt that the derivation was mechanical is that it depended on probability considerations. But Uffink has pointed out that Boltzmann used a frequentist conception of probability, defining the probability that the state of a particle lies within a certain range simply as the relative number of particles whose state lies within that range, and that therefore, the probabilities that are used “can be fully expressed in mechanical terms” (Uffink, 2007, p. 967).

Boltzmann was confronted with the reversibility problem when his good friend Loschmidt discussed the reversibility of mechanical processes in his 1876 article. Boltzmann immediately realized how problematic this issue was for his H-theorem. He wrote a reaction (Boltzmann, 1877) in which he gave a clear formulation of the reversibility problem, and pointed out that it leads to the conclusion that any attempt to give a general mechanical derivation, independent of initial conditions, of the fact that entropy can only increase “must necessarily be futile” (Boltzmann, 1877, p. 365). Yet he immediately added: “One sees that this conclusion has great seductiveness and that one must call it an interesting sophism”, and subsequently set out to find the “source of the fallacy in this argument”. This he did by arguing, like Maxwell and Thomson, that the second law of thermodynamics has a statistical validity, and that although processes in which entropy decreases are theoretically possible, increase of entropy is much more likely than decrease. And, like Maxwell and Thomson, Boltzmann did not seem to perceive this new interpretation of the second law as a weakening of it: it was still a reliable statement, though it was a statistical instead of absolute law of nature (Boltzmann, 1877, p. 366).

However, giving a mechanical derivation of the statement that entropy is more likely to increase than to decrease also turned out to be problematic. The reversibility problem shows that for all initial conditions leading to a process of increase of entropy, other initial conditions can be found which lead to a decrease of entropy; thus, to derive a statistical version of the second law one had either to show or to assume that certain initial conditions, although physically possible, were less probable than others. It was disputable whether one could still claim to have given a mechanical derivation of the second law if the derivation depended on such assumptions. The German mathematician Ernst Zermelo argued against Boltzmann that as long as you cannot explain *why* certain initial conditions are less probable than others, you have actually proven nothing: “as long as one cannot make comprehensible the *physical origin* of the initial state, one must merely assume what one wants to prove” (Zermelo, 1896b, p. 409). To give some plausibility to his claim that certain initial conditions were more probable than others, Boltzmann put forward the argument that the universe as a whole was initially in a very exceptional low-entropy condition and is now still in a process of increase of entropy, and that systems which at a certain moment become isolated from the rest of the universe usually have an exceptionally low-entropy initial condition as well, so that their entropy is more likely to increase than to decrease. Through this assumption the second law can be “explained mechanically”. The low-entropy initial state of the universe then remains unexplained, but Boltzmann argued that “one can never expect that the explanatory principle must itself be explained” (Boltzmann, 1897, p. 413). Whether this was a satisfactory mechanical foundation of the second law still remained a point for discussion.

After Boltzmann's claim that the second law had only statistical validity in (1877), the status of his H-theorem remained uncertain for some period. It was supposed to be a purely mechanical and rigorous derivation of the law of increase of entropy, but this was something that Boltzmann no longer thought to be possible. Yet, at the beginning of the 1890s, the H-theorem was still sometimes used without reservations, for example in Burbury (1890, p. 299ff) and Watson (1893, p. 42ff). For those who did realize that there could be no strictly mechanical derivation of the H-theorem, it was unclear what could be wrong with the derivation that Boltzmann had given.

This matter was resolved in the 1890s in a debate in *Nature* between a number of physicists, namely Burbury, Bryan, Culverwell, Larmor, Watson, and Boltzmann (see Dias, 1994). It became clear that Boltzmann's derivation of the H-theorem depended on an assumption about collisions that was not time symmetric, an assumption that is now known as the Stosszahlansatz. It says that for any two colliding molecules the initial velocities are independent, while the velocities after the collision may be correlated. One has to assume that this holds in order to prove the H-theorem, but if it holds for a certain process, then it fails for the reversed process. The question of where time asymmetry entered in the derivation of the H-theorem was now solved. Moreover, one could argue that the Stosszahlansatz does hold in ordinary gases, and under this assumption, it is possible to give a strict and rigorous derivation of the H-theorem. Boltzmann did exactly this in his *Vorlesungen über Gastheorie* (Boltzmann, 1896, p. 38): he argued that the Stosszahlansatz holds in any system that is “molecularly disordered”, and that molecular disorder is the natural state of gases (see also Kuhn, 1978, p. 66).

One may think that the assumption of molecular disorder amounts to the introduction of a fundamental randomness, but Kuhn (1978, pp. 66–67) points out that this is not correct. If a molecular distribution were picked completely at random, there would be a non-zero probability that it would accidentally be “ordered” and in this case the Stosszahlansatz would not hold. The assumption of molecular disorder instead amounts to the assumption that “ordered” states do not occur at all. We can see that this assumption is quite unnatural. Shortly after its introduction, the assumption was criticized by Zermelo, who argued that while molecular disorder may be acceptable as an assumption about the initial state of a system, one cannot simply assume that it also holds for later states because these later states are determined by the initial state, so whether it holds or not needs to be calculated (Zermelo, 1896b, p. 410).

Thus, it turned out that one could derive either a statistical version of the second law through assumptions about low-entropy initial conditions, or an absolute version of the second law through the assumption of molecular disorder. Both types of assumption were controversial and, in both cases, it was unclear whether the result was a genuine mechanical derivation of the second law. Reconciling mechanism and irreversibility therefore remained problematic.

9. Reversibility and the decline of the mechanistic world view

In Britain, the discussion about the reversibility problem centered on the question of what kind of assumptions should be adopted in order to account for the second law within the kinetic theory of gases: statistical considerations, assumptions about molecular disorder or assumptions about the aether, the latter being proposed by E. P. Culverwell in 1890 as a possible way to account for irreversibility (Culverwell, 1890). Though these different possibilities could have consequences for whether the second law should be regarded as an absolute or statistical law of nature, and for the extent to which the kinetic theory of gases remained mechanistic, neither the second law nor mechanism were questioned in these discussions. When a committee that was appointed by the British Association to investigate “the present state of our knowledge of Thermodynamics, specially with regard to the Second Law” delivered its first report, in 1891, it expressed satisfaction with Boltzmann's statistical explanation of the second law (Bryan, 1892).

Meanwhile, the developments on the continent were rather different. There, in the 1890s, a number of physicists used the reversibility problem to argue against mechanism in physics. In the remainder of this paper, I will focus on their arguments.

Towards the end of the nineteenth century, mechanism in physics received increasing criticism. Mechanical models had played a major role in physics throughout the nineteenth century, but now many physicists such as Duhem and Poincaré felt that certain mechanistic theories had become too complex, involving purely hypothetical yet overly-detailed mechanical models, which were not as fruitful as one would wish. Critics of the mechanistic world view argued that it was better to base science on empirical principles than on speculative mechanistic hypotheses. A key influence was Ernst Mach, who had argued in 1872 that physics should limit itself to describing the “Erkenntniss des Zusammenhanges der Erscheinungen” (Mach, [1872] 1909, pp. 25–26).[14]

As an example of a mechanical theory that had become too speculative and too little fruitful, the kinetic theory of gases was often brought up. In a lecture he held in 1891, Max Planck said of the kinetic theory:

> …bei jedem Versuch, diese Theorie sorgfältiger auszubauen, haben sich die Schwierigkeiten in bedenklicher Weise gehäuft. Jeder, der die Arbeiten derjenigen beiden Forscher studiert, die wohl am tiefsten in die Analyse der Molekularbewegungen eingedrungen sind: Maxwell und Boltzmann, wird sich des Eindrucks nicht erwehren können, dass der bei der Bewältigung dieser Probleme zu Tage getretene bewunderungswürdige Aufwand von physikalischem Scharfsinn und mathematischer Geschicklichkeit nichts im wünschenswerten Verhältnis steht zu der Fruchtbarkeit der gewonnenen Resultate (Planck, 1891a, p. 373; Planck, 1958).[15]

In 1895 the French physicist and philosopher of science Pierre Duhem wrote that while the kinetic theory of gases had originally been received with high expectations, currently disappointment dominated (Duhem, 1895, pp. 852–853). The kinetic theory of gases had started from a quite general idea, namely that heat is a form of motion, but it had grown into a detailed theory to which had been added many assumptions about things that could not be known. Duhem complained that the kinetic theory of gases led to few new results that couldn't have been derived in pure thermodynamics.

In addition, Duhem argued that there were problems with the kinetic theory of gases that still remained unsolved. One was that the theory led to a prediction for the ratio between the specific heat of a gas under constant pressure and the specific heat under constant volume, and that this value was different from the value that was found experimentally (Duhem, 1895, p. 862). This “specific heats problem” had appeared already in an early stage of the kinetic theory: Maxwell had mentioned it in 1860 and had said that it “overturns the whole hypothesis” of the mechanical nature of heat (Maxwell, 1860, p. 660). In the following years various molecular models had been proposed to account for the experimentally obtained ratio of specific heats, but none had become generally accepted, and the problem remained unsolved until the 20th century.

Another problem with the kinetic theory of gases was the problem with accounting for the second law of thermodynamics. In 1892, Duhem had argued that it may well turn out to be impossible to reduce all physical notions and laws to mechanical concepts. He gives an analogy of an artist who can only make pencil sketches: for such an artist it is impossible to represent color. “N'est-ce pas pour une raison analogue que les théories mécaniques les plus complexes n'ont pu, jusqu'ici, rendre un compte satisfaisant du principe de Carnot?” (Duhem, 1892, pp. 156–157).[16]

In 1895, Duhem wrote that despite the efforts that had been made in the kinetic theory of gases by among others Clausius and Boltzmann, the theory was ultimately not very successful exactly because it could not give an account of irreversibility:

> …sans entrer dans des détails techniques qui ne seraient pas de mise en cette étude, reconnaissons qu'elles sont parvenues à rattacher aux lois de la dynamique les propriétés des transformations réversibles, non sans donner prise à quelques critiques et à quelques objections; mais avouons qu'elles n'ont pu,

[14] “knowledge of the connections between observable phenomena”.

[15] “With every attempt to build up the [kinetic] theory more elaborately, the difficulties have mounted in a serious way. Everyone who studies the works of the two investigators who probably have penetrated most deeply into the analysis of molecular motions, namely Maxwell and Boltzmann, will be unable to avoid the impression that the admirable expenditure of physical ingenuity and mathematical skill that they have shown in their attempts to master these problems are not in proportion to the fruitfulness of the results achieved.”

[16] “Is it not for an analogous reason that the most complex mechanical theories have not been able, up to now, to give a satisfactory account of Carnot's principle?” Translation: Duhem (1996, pp. 13–14).

jusqu'ici, rendre compte des propriétés des modifications non réversibles – c'est-à-dire de toutes les modifications réelles. (Duhem, 1895, p. 852).[17]

Duhem contrasted the general disappointment about the kinetic theory of gases with the success of thermodynamics. Thermodynamics became popular around this time as a phenomenological domain of physics, based solidly on observable phenomena and empirical principles. According to Duhem, thermodynamics "était adulte et vigoureusement constituée lorsque les modèles mécaniques et les hypothèses cinétiques sont venues lui apporter un concours qu'elle ne réclamait point, dont elle n'avait que faire et dont elle n'a tiré aucun parti" (Duhem, [1906] 1997, p. 139).[18]

But one has to note that most physicists did acknowledge that the kinetic theory of gases had been very successful in the recent past, and that despite the negative statements made about it, its popularity in practice was probably less damaged than it now seems. Work on the kinetic theory of gases continued throughout the 1890s. Boltzmann, the main proponent of the kinetic theory, greatly complained about the lack of recognition he received during these years; but Uffink (2004) has pointed out that he was in fact a well-respected and much-honoured theoretical physicist. And, in general, those who criticized mechanism often didn't completely condemn it but acknowledged that mechanical pictures and analogies could be useful as a means of research, though one should be careful not to adopt them as truths.[19]

10. Reversibility and recurrence

In 1893, Henri Poincaré argued that reversibility, which is "a necessary consequence of all mechanistic hypotheses", is in contradiction with our daily experience of irreversible phenomena. If this difficulty is not overcome, he argued, it means a definite condemnation of the mechanistic world view. And to strengthen this point he put forward a second, completely new, argument for the incompatibility between mechanism and irreversibility, now known as the recurrence objection. The argument is based on a theorem that he had derived a few years earlier, which says that any bounded dynamical system will, after a certain time (which may be extremely long), almost certainly return to a state that is arbitrarily close to its initial state. Poincaré had derived this theorem in order to prove that our solar system is stable: he could show with this theorem that it is practically certain that the sun, earth and moon will return to positions close to their current position for infinitely many times to come. But he later realized that the theorem also applies to a gas conceived as a mechanical system consisting of molecules: it then says that this system will practically always return to its initial state, which is contrary to the expectation that it will evolve towards a stable and permanent equilibrium state. And if you regard the universe as a whole as a mechanical system, it follows from the recurrence theorem that the universe cannot be irreversibly approaching a state of heat death.

In his *Thermodynamique* (Poincaré, 1892a), Poincaré had deliberately ignored Boltzmann's statistical explanation of the second law, and when Peter Guthrie Tait criticized him in a review for this omission (Tait, 1892), Poincaré responded that the omission was made on purpose:

> Je n'ai pas parlé de cette explication, qui me parâit d'ailleurs assez peu satisfaisante, parce que je désirais rester complètement en dehors de toutes les hypothèses moléculaires quelque ingénieuses qu'elles puissent être; et en particulier j'ai passé sous silence la théorie cinétique des gaz (Poincaré, 1892b).[20]

But in 1893, Poincaré did mention the statistical interpretation of the second law that had been proposed by "the English", calling it the most serious attempt so far to reconcile mechanism and experience (Poincaré, 1893, p. 379). Poincaré did not seem to expect that "the English" would be impressed by the recurrence theorem: they can still argue that the universe is approaching a state of heat death, as long as they admit that this state is not an everlasting final state, but "a sort of slumber, from which it will awake after millions of millions of centuries." Poincaré admitted that this reasoning would be consistent with both the recurrence theorem and experience. He continues:

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.

> One would like to be able to stop at this point and hope that some day the telescope will show us a world in the process of waking up, where the laws of thermodynamics are reversed (Poincaré, 1893, p. 380).

As Brown, Myrvold and Uffink (2009, p. 178) remark, "It is hard not to wonder whether there is a hint of irony here on Poincaré's part". Poincaré did not think he had a definitive answer to "the English", a definitive way to show that mechanism could not account for the irreversibility that we observe. Nevertheless, in the conflict between mechanism and irreversibility he clearly chose in favor of the latter. Whether or not his argument was definitive, it was clear to Poincaré what the most logical conclusion was:

> …there is no need for a long discussion in order to challenge an argument of which the premises are apparently in contradiction with the conclusion, where one finds in effect reversibility in the premises and irreversibility in the conclusion (Poincaré, 1893, p. 380).

A few years later the German mathematician Ernst Zermelo, famous for his work on set theory, also applied Poincaré's recurrence theorem to the issue of mechanism and irreversibility. At this time he was an assistant of Planck, and he agreed with Planck that the second law needed to have an absolute validity rather than a mere statistical validity. While Zermelo had read about Poincaré's theorem in relation to the stability of the solar system, he was actually unaware of the fact that Poincaré had also applied it to the kinetic theory of gases, and even remarked that although Poincaré must certainly be interested in this issue he "does not seem to have noticed [the applicability of his theorem] to systems of molecules or atoms and thus to the mechanical theory of heat" (Zermelo, 1896a, p. 383).

Zermelo's treatment of the recurrence theorem in relation to the kinetic theory of gases was more thorough than that of Poincaré. He noted that the recurrence theorem showed that for

[17] "without entering into technical details, which would be out of place in this study, let us acknowledge that they were able to connect the laws of dynamics to the properties of reversible transformations, though not without giving rise to certain criticisms and certain objections; but let us admit that so far, they have failed to account for the properties of irreversible processes—that is, all actual processes."

[18] "had reached maturity and constitutional vigor when mechanical models and kinetic hypotheses came to give it assistance for which it did not ask, with which it had nothing to do, and to which it owed nothing".

[19] See for example Mach (1896, p. 362), Poincaré ([1905] 1952), p. xvi).

[20] "I have not spoken of this explanation, which by the way seems to me hardly satisfactory, because I wanted to stay completely outside of all molecular hypotheses however ingenious they might be; and in particular I passed over the kinetic theory of gases in silence."

almost all initial states of a mechanical system, the system will return, after a certain time, to a state that is arbitrarily close to its initial state (provided that positions and velocities cannot extend to infinity), and there can therefore be no irreversible processes and no monotonically increasing entropy function. There are a few initial states for which the system does not return to its initial state and for which irreversible processes are possible, but these are singular states whose number is "vanishingly small" compared to the others; in modern terminology, they form a set with measure zero. Zermelo did mention the possibility that only these singular states are "actually realized in nature", but he did not think that this assumption was justified. As we have seen in section 8, Zermelo thought that one could not simply assume that certain initial conditions did not occur as long as one could not explain *why* they did not occur.

> Though such an assumption would be irrefutable, it would hardly correspond to our requirement for causality; and in any case the spirit of the mechanical view of nature itself requires that we should always assume that all *imaginable* mechanical initial states are physically *possible*, at least within certain limits, and certainly we must allow those states that constitute an overwhelming majority and deviate by an arbitrarily small amount from the ones that actually occur (Zermelo, 1896a, p. 389).

According to Zermelo, Poincaré's recurrence theorem showed more convincingly than the reversibility argument that a mechanical derivation of the second law was impossible.[21] He concluded:

> It is now necessary to formulate either the Carnot–Clausius principle or the mechanical theory in an essentially different way, or else give up the latter theory altogether (Zermelo, 1896a, p. 390).

Apparently, giving up the former, the second law, was not an option. Just like Poincaré, he trusted the second law more than the kinetic theory of gases. In fact, like Poincaré, he already had an antipathy of mechanical explanations before he wrote about the recurrence theorem. Ebbinghaus (2007, p. 8) mentions that two years before Zermelo's article about the recurrence theorem was published, in 1894, he had obtained a Ph.D. in mathematics at the Friedrich Wilhelm University in Berlin and, as a part of the procedure, had to defend three theses of his own choice in an oral examination. The second thesis he chose was: "Mit Unrecht wird der Physik die Aufgabe gestellt, alle Naturerscheinungen auf Mechanik der Atome zurückzuführen".[22] With the recurrence theorem, he found a new way to argue for this position.

11. Reversibility, the second law, and empirical principles

In the 1890s, there was still a certain degree of ambiguity about what exactly the second law of thermodynamics was, and thus the relevance of the reversibility problem to the second law was similarly unclear. Many of those who used the reversibility principle to argue against mechanism tended to claim, as did Zermelo, that mechanism failed because it couldn't account for the second law. Another example is František Wald, a relatively unknown and largely uninfluential chemist who had studied technical chemistry in Prague around 1880 and subsequently worked in industrial chemistry. In 1907 he became a professor at the Czech Technical University (Ruthenberg, 2007). In 1889, he published a book about the second law of thermodynamics, which according to him received too little recognition (Wald, 1889). Just like Loschmidt, Wald thought that the second law was counterintuitive in the context of the kinetic theory of gases, since, if heat is nothing more than a kind of motion, the only difference between heat and other kinds of motion is that the former is the unordered motion of molecules. This makes the second law equivalent to the proposition that unordered motion cannot be converted into ordered motion without compensation. But Wald suspected that there were many ways in which this proposition could be violated, for example through Maxwell's demon, who is able to convert unordered motion into ordered motion by manipulating individual molecules and can therefore convert heat into mechanical motion. According to Wald, this possibility would have enormous implications:

> Ein am Boden liegender Stein hat Molekularbewegung – ergo könnte er ohne äussere Arbeitsleistung in die Luft hinaufsteigen. Jeder Eisenbahnzug hat auch ohne Lokomotive genug Wärme – wozu brauchten wir Lokomotiven? Wozu Maschinen, wozu Kohlenwerke? Wärme finden wir überall (Wald, 1889, p. 104).[23]

Wald thought that the possibility of Maxwell's demon was fatal to the attempt to bring the second law into accordance with the kinetic theory of gases. Maxwell had argued that the demon could only violate the second law on a microscopic scale and that it is not possible for us to cause such a violation because we cannot observe and manipulate individual molecules. But Wald argued that it was rather ad hoc to introduce assumptions explicitly in order to make sure that Maxwell's demon cannot operate on an observable scale. Someone might come up with a new thought experiment in which the second law was violated, and then we can do nothing but put forward the hypothesis that such a violation is not possible in practice. Such ad hoc assumptions were inadequate for the foundation of the second law, Wald thought. Thus, he criticized the kinetic theory of gases because it could not give a strong foundation for the second law of thermodynamics, which he valued highly as a law of nature.

But in the 1890s there were still treatments of the second law according to which it was inapplicable to irreversible processes. One example is the version presented in Mach (1892). Mach proposed generalizing the second law to the statement that "jede Umwandlung einer Energieart A ist an einen Potentialfall dieser Energieart gebunden" (p. 1598).[24] This statement does not involve irreversibility, and it is exactly for this reason that Mach thought that the second law could be generalized to be applicable to other domains of physics.

A few years later, in *Principien der Wärmelehre* (1896), Mach gave a different treatment of the second law, and this time he did connect it to irreversible increase of entropy. In a chapter titled "Der Gegensatz zwischen der mechanischen und der phänomenologischen Physik",[25] Mach discussed the mechanical foundations for the second law of thermodynamics. He wrote:

> Bedenkt man, dass ein wirkliches Analogon der *Entropievermehrung* in einem rein mechanischen System aus absolute elastischen Atomen nicht existirt, so kann man sich kaum des Gedankens erwehren, dass eine Durchbrechung des zweiten

[21] A comparison of the strength of the reversibility and recurrence objections is given in Brown et al. (2009, p. 181).

[22] "It is not justified to confront physics with the task of reducing all natural phenomena to the mechanics of atoms."

[23] "A stone lying on the ground has molecular motion—ergo, it could go up in the air without external work being applied to it. Every train also contains enough heat without a heat engine—for what do we need heat engines? For what do we need machines or coal mines? We can find heat everywhere."

[24] "every conversion of a form of energy A is connected to a drop in potential of that form of energy".

[25] "The opposition between mechanical and phenomenological physics"

Hauptsatzes - auch ohne Hülfe von Dämonen - möglich sein müsste, wenn ein solches mechanisches System die *wirkliche* Grundlage der Wärmevorgänge wäre (Mach, 1896, p.364).[26]

Mach made clear that the problem with accounting for entropy increase in mechanistic theories was a problem for mechanism, while the principle of increase of entropy remained well-established as an empirical principle. According to Mach, the existence of irreversible processes was essential for our notion of time. Suppose that all energy conversions could also occur in the reverse direction and all processes could be reversed, "Dann wäre die Zeit selbst umkehrbar, oder vielmehr, die Vorstellung der Zeit hätte gar nicht entstehen können" (Mach, 1896, p. 338).[27] It was not the second law specifically that was important for Mach, but empirical principles in general; empirical principles should form the foundations of physics.

12. Reversibility and energetics

Energetics was a movement that emerged in the 1890s with the goal of unifying natural science by founding it upon the energy concept. It was meant to provide an alternative to the mechanistic world view and intended to be a phenomenological and anti-hypothetical science (Nyhof, 1988, p. 90ff; Deltete, 2007a, p. 6ff). For Wilhelm Ostwald, the main proponent of energetics, the concept of energy was far more important than the concept of entropy, and this led him to devise his own versions of the second law in terms of energy. In the course of time, he gave various accounts of the second law of thermodynamics, which all centered on the question of under which conditions energy changes or conversions occur but were very different in other respects, as Deltete (2007b, p. 303) shows. One can well argue that Ostwald misunderstood the second law of thermodynamics. In a letter to Boltzmann from 1892, Ostwald wrote that the second law had nothing to do with dissipation of energy or with increase of entropy (Ostwald, 1892). He didn't think that there was a relevant principle of increase of entropy, and for Ostwald the second law was not even connected to irreversibility.

In a personal letter, Max Planck expressed his worries to Ostwald about the minor place that he gave to irreversibility in his theory of energetics:

> Der Fortsetzung Ihrer Energetik sehe ich mit großem Interesse entgegen, kann Ihnen aber meine feste Ueberzeugung nicht verhehlen, daß eine alle Naturprozesse umfassende Darstellung sich nicht ausführen lassen wird ohne die *principielle* Unterscheidung zwischen reversibeln u. irreversibeln Prozessen (Planck, 1891b).[28]

Planck gradually lost patience with energetics, which, despite its strong claims of reforming natural science, did not lead to theoretical progress. In 1896 Planck published a firm critique titled "Gegen die neuere Energetik"[29] (Planck, 1896; Planck, 1958; cf. Hiebert, 1971), in which he again emphasized that Ostwald's energetics failed to give an account of irreversibility. Therefore, he argued, the domain of energetics is limited to the study of reversible processes, which includes important parts of mechanics, electrodynamics and optics, but does not include chemistry or thermodynamics (ironically, since energetics was supposed to be anti-mechanistic and close to thermodynamics).

But while irreversibility did not play a central role in Ostwald's physics and specifically played no role in his versions of the second law, this did not mean that irreversibility was not an issue for him. In September 1895, in a lecture titled "Die Überwindung des wissenschaftlichen Materialismus",[30] Ostwald had even used the reversibility problem as an argument against mechanism. He emphasized that the mechanistic world view was incompatible with our daily experience of irreversible processes:

> … die theoretisch vollkommenen mechanischen Vorgänge können ebenso gut vorwärts wie rückwärts verlaufen. In einer rein mechanischen Welt gäbe es daher kein Früher oder Später im Sinne unserer Welt; es könnte der Baum wieder zum Reis und zum Samenkorn werden, der Schmetterling sich in die Raupe, der Greis in ein Kind verwandeln (Ostwald, 1895, p. 230).[31]

Ostwald drew a strong conclusion:

> Die tatsächliche Nichtumkehrbarkeit der wirklichen Naturerscheinungen beweist also das Vorhandensein von Vorgängen, welche durch mechanische Gleichungen nicht darstellbar sind, und damit ist das Urteil des wissenschaftlichen Materialismus gesprochen (Ostwald, 1895, p. 230).[32]

This being said, Ostwald went further to discuss the more promising prospect of energetics. So he used the reversibility problem as a decisive argument against the mechanistic and materialistic world view. He did not argue that the reversibility of mechanical motion was in conflict with the second law; instead he argued that it was in conflict with our direct experience of irreversible processes, of growth and decay.

Ostwald's fellow energeticist Georg Helm was, however, more nuanced. Helm was a German physicist and mathematician, mainly known for being a proponent of energetics but otherwise little influential. Like many other physicists in the 1890s, Helm expressed a dislike for mechanism and the kinetic theory of gases. In his book *The historical development of energetics* (Helm, [1898] 2000), Helm argues that one should not strive for mechanical explanation of all physical phenomena. He adds that the use of mechanical analogies in science can, in certain cases, be quite fruitful, but one should realize that they are based on speculation and should not suppose them to be literally true. Helm complains that "It just seems everywhere to be the fate of mechanical hypotheses that they require too many accessories". In the end, the thermodynamic approach is "more perfect and consistent" than the mechanistic one, for this approach is simpler and needs fewer assumptions. (Helm, [1898] 2000, p. 381, 400; cf. Deltete, 1999).

The very last section of his book is titled "The limits of description by means of mechanical pictures" and begins with the statement that it is problematic to account for the second law of thermodynamics within a mechanistic theory, mainly because it is problematic to account for irreversible processes. However,

[26] "If one realizes that a real analogy of entropy increase in a purely mechanical system, consisting of absolutely elastic atoms, does not exist, one can hardly help thinking that a violation of the second law would have to be possible, also without the help of demons, if such a mechanical system were the real basis of thermal processes."

[27] "Then time itself would be reversible, or rather, the notion of time could not have arisen".

[28] "I look forward with great interest to the continuation of your science of energetics, but I cannot conceal my firm conviction that a comprehensive description of all natural processes cannot be made without the fundamental distinction between reversible and irreversible processes."

[29] "Against the more recent energetics"

[30] "The overcoming of scientific materialism"

[31] "…the theoretically completely mechanical processes can equally well take place forwards as backwards. Therefore, in a completely mechanical world there can be no earlier or later in the sense of our world; a tree might turn back into a twig and into a seed, a butterfly might change into a caterpillar, an old man into a child."

[32] "Thus, the actual irreversibility of real natural phenomena proofs the existence of processes which cannot be derived from mechanical equations, and thereby the verdict of scientific materialism is spoken."

Helm argues that this problem can be solved in a satisfactory manner through statistical considerations, and he seems to be quite convinced by Boltzmann's statistical approach, even if it entails that the spontaneous reversal of an "irreversible" process is not impossible but merely highly unlikely:

> …for the sake of the mechanical hypothesis, one must also accept into the bargain that the course of the world is occasionally reversed. And one must therefore also accept that, in the fullness of time, children will one day return to their mothers' wombs – if one wishes to have the proud feeling that child-bearing follows from conservative forces in accordance with Lagrange's differential equations.
>
> It would certainly be foolish and unjust to want to prove, with this absurdity, that the mechanical world-view is simply a failure. (Helm, [1898] 2000, p. 398).

It might be "foolish and unjust" to argue that mechanism was a failure because it could not account for irreversible processes; meanwhile, this was exactly what Ostwald had done only three years earlier and what also other authors such as Duhem, Poincaré and Zermelo had done. Helm was critical of mechanism, but he thought that the reversibility problem could not be used as an argument against it because the probability of a reversal might be so small that we actually never observe one. The reversibility problem is only an argument against mechanism or the kinetic theory of gases for someone who holds that the second law of thermodynamics is universally valid or that there are fundamentally irreversible processes, even though this conviction goes beyond empirical evidence.

13. Planck's problematic position

According to Max Planck, the second law was fundamental to the understanding of all irreversible processes.[33] In his dissertation from 1879, he had proposed that the entropy function could be regarded as the unique function determining the direction of natural processes: a spontaneous process is only possible in the direction in which entropy increases or remains equal, and not in the direction in which entropy decreases (Planck, 1879). With this in mind, Planck worked on extending the scope of the entropy function, allowing it to become, for example, applicable to chemical processes (see for example Planck, 1887b; Planck, 1958).

But Planck was also committed to mechanism. Although he also warned against a dogmatic attachment to the mechanistic world view, in general he thought that mechanical explanation was an ideal to strive for in physics, and thought that this method "sich bisher in der That überall glänzend bestätigt [34] (Planck, 1887a, p. 51; Kuhn, 1978, pp. 21–22).

By insisting on maintaining both mechanism and irreversibility, Planck placed himself in a problematic position. As early as 1882 he had mentioned a tension between atomism and the second law:

> Der zweite Hauptsatz der mechanischen Wärmetheorie, consequent durchgeführt, ist unverträglich mit der Annahme endlicher Atome.[1] Es ist daher vorauszusehen, dass es im Laufe der weiteren Entwicklung der Theorie zu einem Kampfe zwischen diesen beiden Hypothesen kommen wird, der einer von ihnen das Leben kostet. Das Resultat dieses Kampfes jetzt schon mit Bestimmtheit voraussagen zu wollen, wäre allerdings verfrüht, indeß scheinen mir augenblicklich verschiedenartige Anzeichen darauf hinzudeuten, daß man trotz der großen bisherigen Erfolge der atomistischen Theorie sich schließlich doch noch einmal zu einer Aufgabe derselben und zur Annahme einer continuirlichen Materie wird entschließen müssen (Planck, 1882, p. 475).[35]

The footnote 1 refers to Maxwell's *Theory of Heat* (Maxwell, [1871] 1970), in which Maxwell wrote that the second law "is undoubtedly true as long as we can deal with bodies only in mass and have no power of perceiving or handling the separate molecules of which they are made up", but that it might be violated by the demon. Apparently, it was not the reversibility problem but Maxwell's demon which led Planck to the conclusion that the universal validity of the second law was incompatible with the kinetic theory, and this was probably the reason he thought that it was specifically incompatible with atomism and not necessarily with mechanism. This made things easier for him: to save the second law, he did not have to give up mechanism but only atomism. And in this period he was not very enthusiastic about atomism anyway, since he thought atomic and molecular theories to be somewhat speculative. In fact, his scientific work did involve atoms and molecules, but, according to Heilbron (1986, p. 14), this was only because he found that "he could not stay at the forefront of thermochemistry without recourse to a molecular view of matter", despite his hopes that it would become possible at some point to avoid such molecular hypotheses.

In a letter to his friend Leo Graetz, in 1897, Planck complained that the kinetic theory of gases could not account for irreversibility and was therefore incapable of providing a foundation for the second law of thermodynamics.[36] He opposed a statistical interpretation of the second law; this law had to be a universal principle, a true law of nature, therefore its validity could not be merely highly probable.

He also opposed Zermelo's view that the second law was in contradiction with mechanism in general.[37] Contrary to Zermelo, Planck still had hopes for reconciliation between mechanics and the second law, and his hopes were directed specifically towards theories of continuous matter instead of molecular theories like the kinetic gas theory.

Between 1897 and 1900, Planck worked on a possible new explanation of irreversibility in the domain of electromagnetism. It was Boltzmann who pointed out to Planck that electromagnetism is based on time-reversible laws, just like the kinetic theory of gases and mechanistic theories in general, and that it is therefore impossible to derive strictly irreversible processes within either of these theories without making time-asymmetric assumptions (Kuhn, 1978, p.77; Needell, 1980). After Boltzmann's criticism, Planck did come up with a new theory about irreversibility in the domain of electrodynamics, based on the hypothesis of "natural radiation". This hypothesis, which Planck proposed in the context of cavity radiation (also called black-body radiation), was in fact analogous to the assumption of molecular disorder that Boltzmann had made in 1896, as Kuhn (1978, p. 80) notes. In both cases, it was assumed that certain quantities were disordered

[33] According to Planck, a process is irreversible when, given the final state, it is not possible to restore the initial state, by whatever means.

[34] "until so far has indeed everywhere splendidly been confirmed".

[35] "The second law of thermodynamics, logically developed, is incompatible with the assumption of finite atoms. Hence it is to be expected that in the course of the further development of the theory, there will be a battle between these two hypotheses, which will cost one of them its life. It would be premature to predict the result of this battle with certainty; yet there seem to be at present many kinds of indications that in spite of the great successes of atomic theory up to now, it will finally have to be given up and one will have to decide in favor of the assumption of a continuous matter."

[36] Max Planck to Leo Graetz, May 23, 1897. The relevant part of the letter is printed in Kuhn (1978, pp. 265–266).

[37] Same as footnote 36.

in order to prove the existence of fundamentally irreversible processes; but it was unclear whether this assumption was justified.

We have seen that in the conflict between mechanism and irreversibility, different physicists made different choices depending on the value they attached to mechanism and irreversibility respectively. Planck was in a problematic position because he highly valued both solid mechanical foundations and the absolute validity of the second law of thermodynamics. He tried hard to reconcile these two convictions. Searching for an alternative explanation for irreversible processes, Planck arrived at an explanation similar to one Boltzmann had used earlier in the context of the kinetic theory of gases. But his attempts to account for irreversibility resulted in new and important work: in 1900, Planck introduced his famous quantum constant in the context of cavity radiation.

14. The reasons for anti-mechanism

On the continent, mechanism and atomism received increasing criticism towards the end of the nineteenth century. There has been some debate in the literature about whether this decrease in popularity of mechanism and atomism was motivated primarily by philosophical concerns, such as empiricism and the wish to avoid speculation about unobservable entities, or by physical concerns, such as the lack of progress made in the kinetic theory of gases and the problems with this theory such as its inability to account for the second law and the specific heats problem.

Clark (1976) has proposed a view based on the methodology of "research programs" described by Imre Lakatos. Clark argues that thermodynamics and the kinetic theory of gases were distinct, rival research programs and that "after some early notable successes", by the 1890s, the kinetic theory of gases was degenerating and no longer progressive. According to Clark, the kinetic theory lost popularity because of scientific difficulties and not because of philosophical preferences. The rival research program of thermodynamics was simply more successful and therefore gained popularity at the expense of the kinetic theory of gases.

Nyhof (1988) has defended the older view that philosophical concerns played the main role in the decline in popularity of the kinetic theory. He argues that the kinetic theory and thermodynamics are "explanans and explanandum respectively" and therefore "cannot be scientific rivals": the kinetic theory is intended to be a mechanical *foundation* for thermodynamics, so when thermodynamics is successful, this success should not harm the kinetic theory (Nyhof, 1988, p. 93). That is, unless one already has doubts about the usefulness of the attempt to give a mechanical foundation for thermodynamics—doubts which generally stem from philosophy of science. The fact that the success of thermodynamics was indeed often used as an argument against the kinetic theory of gases shows that such 'philosophical' doubts were common.

The truth probably lies somewhere in the middle: it is true that there were important physical problems with the kinetic theory of gases which played a role in its decline in popularity, such as the specific heats problem, but at the same time Nyhof is correct in pointing out that the anti-mechanism of, for example, Duhem and Mach was mainly philosophically motivated. An alternative road has been taken by De Regt (1996) who argued that the philosophical views of the participants in the debate influenced their scientific work, so that philosophical and physical factors were in fact intertwined. Furthermore, thermodynamics and the kinetic theory of gases were not as radically separated as this literature may suggest, and figures such as Gibbs, Boltzmann and Clausius made important contributions to both.

What role does the reversibility problem play in this discussion? Clark supports his claim by arguing that one of the reasons the kinetic theory lost popularity was that it could not account for the universal validity of the second law, and he brings this up along with the specific heats problem as the main physical problems connected to the kinetic theory (Clark, 1976, p. 43, 81). As we have seen, it is true that the reversibility problem was raised as a physical objection to the kinetic theory by people such as Duhem, Poincaré and Zermelo. But in fact, whether one regarded the failure of kinetic theory to account for the second law as problematic for the kinetic theory was itself highly dependent on philosophical considerations. The same problem could also be used as an argument against the second law, as Loschmidt had done, or it could be handled through a statistical approach, as Maxwell, Thomson and Boltzmann had done. It was the widespread, philosophically motivated anti-mechanism in the 1890s that determined the interpretation of the reversibility problem as a problem for the kinetic theory of gases. Therefore, when arguing that the decline in popularity of the kinetic theory of gases was motivated primarily by physical concerns, one cannot use the reversibility problem as an example.

15. Conclusion

The reversibility problem was connected with many different issues in physics and philosophy of science. In the first years after the appearance of the reversibility problem, the main factors determining its interpretation were aversions to materialism (Maxwell, Thomson, Breton) and to the idea of the heat death of the universe (Loschmidt), and the development of the idea of statistical laws of nature (Maxwell, Thomson, Boltzmann). In the last decade of the nineteenth century, especially in Germany and France, the discussion about the reversibility problem became primarily a discussion about the merits of mechanism versus empiricism in physics. Should we believe in the unrestricted validity of our laws of nature, should we base our science upon empirical principles, or should we aim at mechanistic reduction? Can thermodynamics stand on its own or does it need the kinetic theory of gases as a mechanical foundation? The answers to these questions determined the interpretation of the reversibility problem, and it was only when mechanism was losing favor in the 1890s that the reversibility problem came out as an objection against it: basically, the reversibility problem could be used as a physical objection to whatever one was philosophically opposed to.

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References

Bierhalter, G. (1992). Von L. Boltzmann bis J. J. Thomson: Die Versuche einer mechanischen Grundlegung der Thermodynamik (1866–1890). *Archive for History of Exact Sciences*, *44*, 25–75.

Boltzmann, L. (1872). Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. *Sitzungsberichte der Akademie der Wissenschaften zu Wien, mathematisch- naturwissenschaftliche Klasse*, *66*, 275–370 (English translation in Brush (2003) pp. 262–349).

Boltzmann, L. (1877). Bemerkungen über einige Probleme der mechanische Wärmetheorie. *Sitzungsberichte der Akademie der Wissenschaften zu Wien, mathematisch-naturwissenschaftliche Klasse*, *75*, 62–100 (Partial English translation in Brush (2003) pp. 362–367 (NB: The title ascribed to this paper in Brush (2003) is not right)).

Boltzmann, L. (1896). *Vorlesungen über Gastheorie*. Vol. 1. Leipzig: Verlag von Johann Ambrosius Barth.

Boltzmann, L. (1897). Zu Hrn. Zermelo's Abhandlung über die mechanische Erklärung irreversibler Vorgänge. *Annalen der Physik*, *60*, 392–398 (English translation in Brush (2003) pp. 412–419).

Breton, P. (1875). De la réversibilité de tout mouvement purement matériel. *Les Mondes*, *38* 566–572, 606–616, 643–648, 697–702, 742–754.

Brown, H. R., Myrvold, W., & Uffink, J. (2009). Boltzmann's H-theorem, its discontents, and the birth of statistical mechanics. *Studies in History and Philosophy of Modern Physics*, *40*(2), 174–191.

Brown, H. R., & Uffink, J. (2001). The origins of time-asymmetry in thermodynamics: The minus-first law. *Studies in History and Philosophy of Modern Physics*, *32*(4), 525–538.

Brush, S. G. (1976). *The kind of motion we call heat*. Vols. 1–2. Amsterdam: North Holland.

Brush, S. G. (2003). *The kinetic theory of gases: An anthology of classical papers with historical commentary*. London: Imperial College Press.

Bryan, G. H. (1892). Report of a committee, consisting of Messrs. J. Larmor and G. H. Bryan, on the present state of our knowledge of Thermodynamics, specially with regard to the Second Law. Part I.—Researches relating to the connection of the Second Law with Dynamical Principles. In *Report of the sixty first meeting of the British Association for the Advancement of Science* (pp. 85–122). London: John Murray.

Burbury, S. H. (1890). On some problems in the kinetic theory of gases. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, *5*(30), 298–317.

Carbonnelle, I. (1881). (3rd ed). *Les confins de la science et de la philosophie*, Vol. 1. Paris, Bruxelles, Genève: Société Générale de Librairie Catholique.

Cercignani, C. (1998). *Ludwig Boltzmann, the man who trusted atoms*. Oxford: Oxford University Press.

Clark, P. (1976). Atomism versus thermodynamics. In: C. Howson (Ed.), *Method and appraisal in the physical science* (pp. 41–105). Cambridge: Cambridge University Press.

Culverwell, E. P. (1890). Note on Boltzmann's kinetic theory of gases, and on Sir W. Thomson's address to Section A, British Association, 1884. *Philosophical Magazine*, *5*(30), 95–99.

De Regt, H. (1996). Philosophy and the kinetic theory of gases. *British Journal for the Philosophy of Science*, *47*, 31–62.

Deltete, R. (1999). Helm and Boltzmann: Energetics at the Lübeck Naturforscherversammlung. *Synthese*, *119*, 45–68.

Deltete, R. (2007a). Wilhelm Ostwald's energetics 1: Origins and motivations. *Foundations of Chemistry*, *9*, 3–56.

Deltete, R. (2007b). Wilhelm Ostwald's energetics 2: Energetic theory and applications, Part I. *Foundations of Chemistry*, *9*, 265–316.

Dias, P. M. C. (1994). Will someone say exactly what the H-theorem proves? A study of Burbury's Condition A and Maxwell's Proposition II. *Archive for History of Exact Sciences*, *46*, 341–366.

Duhem, P. (1892). Quelques réflexions au sujet des théories physiques. *Revue des questions scientifiques*, *31*, 139–177.

Duhem, P. (1895). Les theories de la chaleur. *Revue des Deux Mondes*, *129* 869–901, *130*, 379–415, 851–868.

Duhem, P. ([1906] 1997). La theorie physique: son objet, sa structure. (P. Brouzeng (Ed.)). Paris: Vrin.

Duhem, P. (1996). Essays on history and philosophy of science. (R. Ariew and P. Barker, (Eds.)). Indianapolis, Cambridge: Hackett Publishing.

Ebbinghaus, H. D. (2007). *Ernst Zermelo: An approach to his life and work*. Berlin, Heidelberg: Springer.

Gibbs, J. W. (1876–1878). On the equilibrium of heterogeneous substances. In: H. A. Bumstead, & R. G. Van Name (Eds.), *The scientific papers of J. Williard Gibbs* (Vol. 1). London: Longmans, Green and Co. 1906

Harman, P. M. (1998). *The natural philosophy of James Clerk Maxwell*. Cambridge: Cambridge University Press.

Heilbron, J. L. (1986). *The dilemmas of an upright man: Max Planck as spokesman of German science*. Berkeley: University of California Press.

Helm, G. ([1898] 2000). *The historical development of energetics* (R. J. Deltete, Trans.). Dordrecht, Boston, London: Kluwer Academic Publishers.

Hiebert, E. N. (1971). The energetics controversy and the new thermodynamics In: D. H. D. Roller (Ed.), *Perspectives in the history of science and technology* (pp. 67–86). Norman, Oklahoma: University of Oklahoma Press.

Klein, M. J. (1972). Mechanical explanation at the end of the nineteenth century. *Centaurus*, *17*, 58–82.

Klein, M. J. (1973). The development of Boltzmann's statistical ideas. In: E. G. D. Cohen, & Walter Thirring (Eds.), *The Boltzmann equation: Theory and applications* (pp. 53–106). Wien: Springer-Verlag.

Kragh, H. (2008). *Entropic creation: Religious context of thermodynamics and cosmology*. Aldershot, Hampshire: Ashgate Publishing.

Kuhn, T. S. (1978). *Black-Body theory and the quantum discontinuity* (pp. 1894–1940) Oxford: Oxford University Press1894–1940.

Loschmidt, J. J. (1866). *Zur Theorie der Gase. Sitzungsberichte der Kgl. Akademie der Wissenschaften in Wien, 54*, 646–662.

Loschmidt, J. J. (1867). Die Weltanschauung der modernen Naturwissenschaft. Zwei Vorträge, gehalten am 9. und 16. Dezember 1867. *Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse*, *8*, 42–106.

Loschmidt, J. J. (1869). Der zweite Satz der mechanischen Wärmetheorie. *Sitzungsberichte der Kgl. Akademie der Wissenschaften in Wien*, *59*(2), 395–418.

Loschmidt, J. J. (1876). Über den Zustand des Wärmegleichgewichtes eines Systeme von Körpern mit Rucksicht auf die Schwerkraft. *Sitzungsberichte der Kgl. Akademie der Wissenschaften in Wien*, *73*, 128–142.

Mach, E. ([1872] 1909) *Die Geschichte und Wurzel des Satzes von der Erhaltung der Arbeit. Vortrag gehalten in der K. Böhm. Gesellschaft der Wissenschaften am 15. Nov. 1871* (2nd ed.). Leipzig: Verlag von Johann Ambrosius Barth.

Mach, E. (1892). Zur Geschichte und Kritik des Carnot'schen Wärmegesetzes. *Sitzungsberichte der Mathematisch- Naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften, Wien*, *101*, 1589–1612.

Mach, E. (1896). *Die Principien der Wärmelehre. Historisch-kritisch entwickelt*. Leipzig: Verlag von Johann Ambrosius Barth.

Maxwell, J. C. (1857). In: Harman, P. M. (ed), The scientific letters and papers of James Clerk Maxwell, Vol. 2, (pp. 560–563). Cambridge: Cambridge University Press.

Maxwell, J. C. (1860). On the results of Bernoulli's theory of gases as applied to their internal friction, their diffusion, and their conductivity for heat (summary of a paper delivered to the Oxford meeting of the British Association, 1860). In: P. M. Harman (Ed.), *The scientific letters and papers of James Clerk Maxwell*, Vol. I (pp. 659–660). Cambridge: Cambridge University Press.

Maxwell, J. C. (1868). In: Harman, P. M. (ed), The scientific letters and papers of James Clerk Maxwell, Vol. 2, (pp. 358–361). Cambridge: Cambridge University Press.

Maxwell, J. C. (1870a). Address to the mathematical and physical sections of the British Association. In: W. D. Niven (Ed.), *The scientific papers of James Clerk Maxwell*, Vol. 2 (pp. 215–229). New York: Dover Publications, Inc.

Maxwell, J. C. (1870b). In: P. M. Harman (Ed.), *The scientific letters and papers of James Clerk Maxwell*, Vol. 2 (pp. 582–583). Cambridge: Cambridge University Press.

Maxwell, J. C. ([1871] 1970). *Theory of heat* (3rd ed.). Westport, Connecticut: Greenwood.

Maxwell, J. C. (1873). Essay for the Eranus club on science and free will. In: P. M. Harman (Ed.), *The scientific letters and papers of James Clerk Maxwell*, Vol. 2 (pp. 814–823). Cambridge: Cambridge University Press.

Maxwell, J. C. (1878). Tait's 'Thermodynamics'. In: E. Garber, S. G. Brush, & C. W. F. Everitt (Eds.), *Maxwell on heat and statistical mechanics: On "avoiding all personal enquiries" of molecules* (pp. 276–287). Bethlehem: Lehigh University Press 1995.

Needell, A. A. (1980). *Irreversibility and the failure of classical dynamics: Max Planck's work on the quantum theory, 1900–1915*. Ann Arbor, Michigan: University Microfilms International.

Nyhof, J. (1988). Philosophical objections to the kinetic theory. *British Journal for the Philosophy of Science*, *39*, 81–109.

Ostwald, W. (1892). In: H.-G. Körber (Ed.), *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds*, Vol. 1 (pp. 9–10). Berlin: Akademie-Verlag 1961.

Ostwald, W. (1895). Die Überwindung des wissenschaftlichen Materialismus. In: W. Ostwald (Ed.), *Abhandlungen und Vorträge allgemeinen Inhaltes (1887–1903)*, 1904 (pp. 220–240). Leipzig: Verlag von Veit & Comp.

Planck, M. (1879). *Über den zweiten Hauptsatz der mechanischen Wärmetheorie*. Munich: Theodor Ackermann.

Planck, M. (1882). Verdampfen, Schmelzen und Sublimieren. *Annalen der Physik*, *15*, 446–475.

Planck, M. (1887a). *Das Princip der Erhaltung der Energie*. Leipzig: B. G. Teubner.

Planck, M. (1887b). Über das Princip der Vermehrung der Entropie - Erste Abhandlung. In Planck (1958) (pp. 196–273).

Planck, M. (1891a). Allgemeines zur neueren Entwicklung der Wärmetheorie. In Planck (1958) (pp. 372–381).

Planck, M. (1891b). In: H.-G. Körber (Ed.), *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds*, Vol. 1 (p. 38). Berlin: Akademie-Verlag 1961.

Planck, M. (1896). Gegen die neuere Energetik. In Planck (1958) (pp. 459–465).

Planck, M. (1958). *Physikalische Abhandlungen und Vorträge*. Vol. 1. Braunschweig: Friedr. Vieweg & Sohn.

Poincaré, H. (1892a). *Thermodynamique. Cours de physique mathématique, leçons professées pendant le premier semestre 1888–89*. Paris: Gauthier-Villars.

Poincaré, H. (1892b). Untitled letter. *Nature*, *45* (March 24, 1892), 485.

Poincaré, H. (1893). Le mécanisme et l'expérience. *Revue de Metaphysique et de Morale*, *1*, 534–537 (English translation in Brush (2003) pp. 377–381).

Poincaré, H. ([1905] 1952). *Science and hypothesis*. New York: Dover.

Porter, T. M. (1986). *The rise of statistical thinking 1820–1900*. Princeton, New Jersey: Princeton University Press.

Ruthenberg, K. (2007). František Wald (1861–1930). *HYLE—International Journal for Philosophy of Chemistry*, *13*(1), 55–61.

Smith, C., & Wise, M. N. (1989). *Energy and empire: A biographical study of lord Kelvin*. Cambridge: Cambridge University Press.

Stoney, G. J. (1887). Curious consequences of a well-known dynamical theorem. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, *5* (23), 544.

Tait, P. G. (1892). Poincaré's thermodynamics. *Nature*, *45*, 245.

Thomson, J. J. (1888). *Applications of dynamics to physics and chemistry*. London: Macmillan and co.

Thomson, W. (1852). On a universal tendency in nature to the dissipation of mechanical energy. In: Kelvin (Ed.), *Mathematical and physical papers*, Vol. 1 (pp. 511–514). Cambridge: Cambridge University Press 1882.

Thomson, W. (1874). The kinetic theory of the dissipation of energy. In Brush (2003) (pp. 350–361).

Thomson, W. (1892). On the dissipation of energy. In: Kelvin (Ed.), *Popular lectures and addresses*, Vol. 2 (pp. 451–474). London, New York: MacMillan and Co 1894.

Torretti, R. (2007). The problem of time's arrow historico-critically reexamined. *Studies in History and Philosophy of Modern Physics*, *38*, 732–756.

Uffink, J. (2001). Bluff your way in the second law of thermodynamics. *Studies in History and Philosophy of Modern Physics*, *32*, 305–394.

Uffink, J. (2004). Boltzmann's work in statistical physics. *The Stanford encyclopedia of philosophy*. ⟨http://plato.stanford.edu/entries/statphys-Boltzmann/⟩.

Uffink, J. (2007). Compendium of the foundations of classical statistical physics. In: J. Butterfield, & J. Earman (Eds.), *Handbook of the philosophy of science—philosophy of physics*. Amsterdam: Elsevier.

Wald, F. (1889). *Die Energie und ihre Entwertung. Studien über den zweiten Hauptsatz der mechanischen Wärmetheorie.* Leipzig, Verlag von Wilhelm Engelmann

Watson, H. W. (1893). *A treatise on the kinetic theory of gases* (2nd ed.). Oxford: Clarendon.

Zermelo, E. (1896a). Über einen Satz der Dynamik und die mechanische Wärmetheorie. *Annalen der Physik*, *57*, 485–494 (English translation in Brush (2003) pp. 382–391).

Zermelo, E. (1896b). Über mechanische Erklärungen irreversibler Vorgänge. *Annalen der Physik*, *59*, 4793–4801 (English translation in Brush (2003) pp. 403–411).