Ludwig Boltzmann

The man who trusted atoms

Carlo Cercignani (Oxford UP, 1998)

Preface

xi It is remarkable that, with a few exceptions, Boltzmann's scientific papers have not been translated into English $\cdots$. Because of this, much of Boltzmann's work is known through somebody else's presentation, not always faithful. Yet he was the man who did most to establish the fact that there is a microscopic, atomic structure underlying macroscopic bodies.

Introduction

4 As we shall see, he opposed "idealistic philosophy"; it is interesting to remark that Lenin quotes with approval the views of Boltzmann, who thus became a hero of scientific materialism int he former Soviet Union.

1. A short biography of Ludwig Boltzmann

5 His father's salary was not large but was compensated by his mother's fortune; she[1] came in fact from a rather rich family (in Salzburg there is still a Pauernfeindgasse and even a Pauernfeindstrasse).
In Linz he also took piano lessons from Anton Bruckner. The lesson case to a sudden end when the mother of the future scientist made an unfavorable remark on the fact that the master had put his wet raincoat on a bed.

6 Stefan was one of the few non-British physicists who were receptive to the idea of local action mediated by a field.

8 the objections of friends and adversaries forced him to reshape his ideas and created another view, which is uncompromisingly new and opened a novel era in physics.

13 Boltzmann, who was tender-hearted... Whenever a favor was requested from him, he was not able to say no. $\cdots$ In the last years of his life, no student failed an examination with him.

Thus he (=Mach) was against experimental picture of models that could go beyond observed facts. For this reason he denied the existence of atoms. As we shall see in Chapter 10, Boltzmann's philosophy was different in many details and was very much in favor of pictures, as models of reality helping us in making discoveries.

15 Boltzmann had also bought a farm near Oberkroisbach, with a commanding view over a large part of Styria, and lived in the country with his family. He knew the plants well, had a herbarium and possessed a collection of butterflies.

19 A scientific dispute with two famous British colleagues of his, P.G. Tait and W. Burnside, in 1885-7 contributed considerably to improving his relations with the British physicists. Since not many people dared to read his lengthy papers, it was through these discussions that

[1] Maria Pauernfeind

Boltzmann laid the foundations for his international reputation, which grew perhaps earlier in England than in the German-speaking world.

30 The lectures on philosophy were the most popular lectures by Boltzmann, who, when appointed to that duty, had imagined that philosophy was his true calling. $\cdots$ After two or three sparkling talks, however, his enthusiasm diminished and with this the audience as well.

34 Boltzmann was very proud of his English... Yet the comments of people attending the lectures express some reservations about his command of the language.
It is reported that if he had lectured in German most of his audience might have been able to follow him.....

35 Boltzmann was considered ta great teacher and his audiences got the impression that he was deeply interested in the subject o the lecture and happy to give it. But we know form his assistant Stefan Mayer that lecturing was painful for him and whenever there was a possibility of canceling a lecture, he was more relieved than disappointed.

36 Among the people who were shocked by the new of Boltzmann's death, was Erwin Schrödinger, then about 19 years old. He had expected to begin his studies in theoretical physics within a few months under the great master.

Another person who was frustrated by Boltzmann's suicide was Ludwig Wittgenstein, who, when leaving Linz in 1906, had hoped to learn from him.

37 In Vienna he had among his students Paul Ehrenfest, Fritz Hasenöhrl, Stefan Mayer, Lise Meitner; in Graz, Svante August Arrhenius, Walter Nernst.

38 Boltzmann was fascinated not only by scientific problems, but also by promising scientific inventions.
He was deeply interested in technology and more than once praised the role of technology in the development of science.

43 From the political viewpoint, Boltzmann may be considered to have been a democratic radical and a resigned republican.

46 So, beneath the glittering surface was a society whose members were incapable of opening themselves to others. $\cdots$ Correspondingly the suicide rate was very high. $\cdots$ The list of people who committed suicide in those times is very long and, in addition to Boltzmann includes three elder brothers of Wittgenstein, Otto Weininger, Georg Trackl, Otto Mahler, Alfred Redl, and Eduard van der Nüll.

2. Physics before Boltzmann

51 [Newton's atom was not a point particle] Newton himself in his *Optics* says:

$\cdots$ these primitive particles being solid are incomparably harder than any porous bodies compounded of then; even so very hard, as never to wear of break in pieces; no ordinary power being able to divide what God himself made one in the first creation.

His successor, however, began to think of the atoms as of point masses, between which at least another force, in addition to Newton's attraction, should act.

52 The most systematic treatise of this early atomic theory, which produced some interesting results, is due to Roger Joseph Boscovich (1711-87). His extensive output concerns practically every aspect of science and culture of his time, but his treatise,[2] which is an attempt to understand the universe by means of a unified model, is perhaps the highest point of his researches.

Boscovioch is a typical example of an eighteenth century physicist. If we devote some space to his, it is not only because he was the first who tried to develop a systematic atomic theory in the framework of Newton's mechanics, but also because he exerted a great influence on great physicists of the nineteenth century, such as Faraday, Oersted, Lord Kelvin.

55 [Boscovich's atom was a point particle. Boltzmann wrote]fFor a long time the celebrated theory of Boscovich was ideal of physicists. *cdots* The assumption that the gas-molecules are aggregates of material points, in the sense of Boscovich, does not agree with facts.
Here Boltzmann is referring to the fact that an atom cannot be a simple object, as was amply known in his time from spectroscopy.

We must also remark that Boscovich was the first to assert determinism, though conceding some for free will.

59 We must emphasize the fact that geologists, and in particular James Hutton (1726-97) had opposed the theory of gradual cooling of the earth proposed by Georges-Louis Leclerc, Count Buffon (1707-88). Although Buffon's argument and laboratory experiments were impeccable, given the knowledge of his days, Hutton remarked that a "subterranean fire" must "exist in all its vigor at this day."[3]

60 In 1796m when Lazare Carnot was a member of the Directory of France, his elder son,
Nicholas Léonard Sadi Carnot (1796-1832) was born. A few years later Lazare was Minister
61 of War and he often took his little sone Sadi with him when he visited napoleon. Once
Napoleon was amusing himself throwing stones near a group of ladies (including his wife) who were on a boat on a lake, splashing them. The little boy ran up and shouted at him: "You, beastly First Consul, sop teasing those ladies!" Napoleon laughed and so there was no serious consequence for the history of science.

64 Thermodynamics, which can be regarded as a limitation of our ability to act on the mechanics of the minutest particles of a body, was not enough to complete our description of nature.

3. Kinetic theory before Boltzmann

72 in addition to the fact that it was only qualitative and not quantitative, it contained some basic flaws. The most remarkable one appears to be due to ignorance of the first principle of mechanics, the law of inertial.

[2]R. Boscovich, *Theoria philosophiae naturalis* (1763, Venice); in English *A theory of natural philosophy* (Open Court, Chicago 1922; reprinted from MIT Press, 1966).

[3]J. Hutton, *Theory of the Earth* (Edinburgh, 1795).

In medieval times some Arab thinkers accepted the atomic theory, which on the contrary was fiercely attacked by the scholastic theologies in the West, who maintained that it conflicted with the dogma of transubstantiation. During the Renaissance period, ideas related to atomism occur in the writings of Giordano Bruno (1548-1600), Galileo Galilei (1564-1642), and Francis Bacon (1561-1626).

73 Daniel Bernoulli belonged to a large family of mathematicians and mathematical physicists (their name is sometimes spelt Bernoulli).
74 Among the many Bernoullis, Daniel must be rated as the most profound in the application of mathematics to physical problems.

76 John Herapath (1790-1869) gave the first explicit value for the average speed of a molecule in a gas. James Prescot Joule, to whom this priority is usually attributed, seems to have based his calculation on Herapath's. In many case, their results were astonishing: the average speed of a molecule in hydrogen turned to be about 2 km/s, greater than any velocity that had been met in artillery practice!

77 Clausius had been the first to formulate the Second Law of Thermodynamics and to discover the hidden concept of entropy. His first paper on the kinetic theory of gases, entitled *Über die Art der Bewegung, welche wir Wärme nennen*, which appeared in 1857 in Poggendorff's *Annalen*, defined the scope of most nineteenth century work in kinetic theory.

One of the first scientists to react Clausius' first paper was Stanislao Cannizzaro (1826-1910), who had revived the chemical atomic theory in its modern from based on the hypothesis of Amedeo Avogadro (1776-1856).His widely known *Sunto di un corso di Filosofia Chimica* (1858, reprinted as *Sketch of a Course of Chemical Philosophy* (The Alembin Club, Edinburgh, 1961) was distributed at a meeting in Karlsruhe in 1860 and quoted the new researches ("from Gay-Lussac to Clausius") to support Avogadro' views.

80 In 1860, two years after Clausius had introduced the mean free path on the basis of this concept (= statistical count), James Clark Maxwell (1831-1879) developed a preliminary theory of transport processes such as heat transfer, viscous drag, and diffusion.

81 With his transfer equations (= detailed balance relation), Maxwell had come very close to an *evolution equation for the distribution function*, but this last step must beyond any doubt be credited to Ludwig Boltzmann (1844-1906).

In the science literature before 1850 one finds scattered statements about something that is lost or dissipated when heat is used to produce mechanical work, but only in 1852 did William Thomson asserted the existence of "a universal tendency in nature to the dissipation of mechanical energy." The consequences of Thomson's Principle of Dissipation were elaborated by Helmholtz, who tow years later described the "heat death" of the universe. $\cdots$ It
82 is to be stressed that Clausius had already remarked in 1850 that, although Carnot's argument ca be reconciled with the equivalence of work and heat through a slight modification, something more that the impossibility of perpetual motion had to be invoked as a postulate. In fact neither the First Law (equivalence of heat and work) nor Carnot's argument shows any feature of irreversibility, whereas heat "always shows a tendency to equalize temperature differences and therefore to pass from hotter to colder bodies."

83 This “demon” is described for the first time in a letter from Maxwell to Tait in 1867. But its first appearance in public was in the *Theory of heat* by Maxwell, published in 1871.

84 As remarked by Klein[4] “Maxwell observed this and later disputes over the mechanical interpretation of the second law with detachment—and no little amusement.” In maxwell’s own words:

> It is rare sport to see those learned Germans contending for the priority of the discovery that the 2nd law of $\theta\Delta$cs is the Hamiltonsche Princip, when all the time they assume that the temperature of a body is but another name for the vis viva of one of its molecules...

Why was Maxwell so mocking about “those learned Germans”? Because the prize for which they were contending was an illusion. He knew already, as his discussion of the demon named after him shows, that if heat is motion, then the Second Law “is equivalent to a denial of our power to perform the operation just described, either by a train of mechanisms, or by any method yet discovered.

85 If a scientist of the stature of Maxwell missed the importance of a result offering a way of measuring our inability to transform heat into ordinary motion, then we should be sympathetic to our contemporaries when they are unable to understand the meaning of Boltzmann’s discovery.

4. The Boltzmann equation

86 As remarked by M J Klein[5] Boltzmann interprets Maxwell’s distribution function in two different ways, which he seems to consider as a priori equivalent: the first way is based on the fraction of a sufficiently long *time interval*, during which the velocity of a specific molecule has values within a certain volume element in velocity space, whereas the second way is based on the fraction of *molecules* which, at a given instant, have a velocity in the said volume element. It seems clear that Boltzmann did not at that time feel any need to analyze the equivalence.

87 the total energy E is

$$\langle E\rangle = NT + \langle\chi\rangle \tag{1}$$

where χ is the potential energy. It is then clear that one can change the value of $\rangle E\langle$ in two ways, i.e., by changing either the temperature or the average potential so slowly as to go through equilibrium states, to obtain

$$\delta\langle E\rangle = N\delta T + \delta\langle\chi\rangle, \tag{2}$$

where δ denotes an infinitesimal change. If we denote the heat supplied to the system in the process by $\delta' Q$ and compute it as the difference between the increase in average total energy and the average work done on the system, we have

$$\delta' Q = \delta\langle E\rangle - \langle\delta\chi\rangle = N\delta T + \delta\langle\chi\rangle - \langle\delta\chi\rangle. \tag{3}$$

We remark that $\delta\langle\chi\rangle$ and $\langle\delta\chi\rangle$ are different; in fact, the operation of taking an average will depend on certain macroscopic parameters, typically temperature, which are allowed to

[4] M. Klein, Maxwell, his demon, and the second law of thermodynamics, Am Scientist **58**, 84-97 (1970).

[5] The development of Boltzmann’s statistical idea, in *The Boltzmann equation: theory and applications*, ed E G D Cohen and W Thirring (Springer, 1973).

change in the process under consideration. Thus it is not the same thing if we first average the potential and then look at the change in this average (which depends on temperature) or we first compute the change in χ (which does not depend on temperature) and then average it.

88 The paper of 1872 started with a critique of the derivation of velocity distribution in a gas in an equilibrium state, given by Maxwell, with an emphasis on the fact that that deduction had shown only that the Maxwell distribution, once achieved, is not altered by collisions.However, said Boltzmann, "it has still not yet been proved that, whatever the initial state of the gas may be, it must always approach the limit found by Maxwell."

89 Just a few page of the voluminous memoir by Boltzmann concern the calculation of the transport properties in a gas. It is in these pages however, that Boltzmann laid down his equation in the most familiar form for us.

93 Jus before collision

$$P^{(2)}(\boldsymbol{x}_1, \boldsymbol{v}_1, \boldsymbol{x}_1 + \boldsymbol{n}\sigma, \boldsymbol{v}_2, t) == P^{(1)}(\boldsymbol{x}_1, \boldsymbol{v}_1, t) P^{(1)}(\boldsymbol{x}_1 + \boldsymbol{n}\sigma, \boldsymbol{v}_2, t)) \quad \text{for } (\boldsymbol{v}_2 - \boldsymbol{v}_1) \cdot \boldsymbol{n} < 0. \tag{4}$$

The Boltzmann equation is an evolution equation for $P^{(1)}$, without any reference to $P^{(2)}$ or P. This is its main advantage. However, it has been obtained at the price of several assumptions;the chaos assumption present in eq(4) is particularly strong and requires to be discussed a little.

94 The molecular chaos assumed in eq (4) is clearly a property of randomness.

95

$$P^{(s)}(t) = \prod_{s} P^{(1)}(t) \tag{5}$$

Thus the task becomes to show that, if true at $t = 0$, this property remains preserved (for any fixed s) and for molecules about to collide, in the Boltzmann-Grad limit.
There remains the problem of justifying the *initial chaos assumption.* $\cdots$ The physical reason for this is that in general we cannot handle the single molecules, but rather act on the gas as a whole, usually starting from an equilibrium state(for which (5) holds). The mathematical argument indicates that if we choose the initial data f or the molecules at random, there is an overwhelming probability that eq (5) so satisfied at $t = 0$.
[**C**] Both are quite unconvincing. For the math part Cercignani quotes Boltzmann and Maxwell, useless references for rigorous math. In the following paragraph, he points out:
This clarification from a physical standpoint is due to Ehrenfest, while the problems posed by a mathematically rigorous justification are at the moment only partly solved.

5. Time irreversibility and the H-theorem

97 The H-theorem led to a strange situation, perhaps unique in the history of science: on the one hand, the Boltzmann equation had been successfully applied to a large number of physical phenomena; on the other hand, Boltzmann's ideas met with violent objections put forward by both physicists and mathematicians.
[**C**] 'successfully applied"? Qualitatively yes. Quantitatively yes with adjustable parameters called the intermolecular potentials.

98 The time reversal paradox was first mentioned by Thomson:
This paradox is mentioned by Thomson in a short paper which is seldom quoted.[6] It appeared in 1874 and contains a substantial part of the physical aspect of the modern interpretation of irreversibility, not only for gases but also for more general systems made up of molecules. Thomson notes that

> the instantaneous reversal of the motion of every moving particle of a system causes the system to move backwards, each particle of its old path, and at the same speed as before, when again in the same position. That is to say, in mathematical language, any solution remains a solution when t is changed into $-t$.

Joseph Loschmidt, to whom the paradox is usually attributed, mentioned it in the first of four articles demoted to the thermal equilibrium of a system of bodies subjected to gravitational forces.

99 Probably the two friends had discussed the objection together. This may explain how, in spite of the obscure arguments of Loschmidt, Boltzmann immediately grasped the essential point.
He published a paper in which he pays a handsome tribute to his critic because the doubt about the demonstration of the H-theorem "is ingeniously thought out and seems to be of great importance for a correct understanding of the Second Law." $\cdots$
We remark that in this paper Boltzmann explicitly recognizes the probabilistic nature of the Second law.

100 Cercignani mentions Nietzsche for Zermelo's paradox.

The famous French mathematician is concerned with obstacles met by the "mechanistic conception of the universe which has seduced so many good man". In fact, he says, "a theorem, easy to prove, tells us that a bounded world, governed by the laws of mechanics, will always pass through a state very close to its initial state". After noting the contradiction with the Second Law, he goes on to say (apparently ignoring Boltzmann):

> According to this theory, to see heat pass fro a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and dexterity of Maxwell's demon; it will suffice to have a little patience.

Thus Poincare was fighting against the idea that everything can be reduced to the motion of atoms.

101 In 1896 Zermelo, starting from this memoir of Poincare's and ignoring the latter's short paper [17], gives a short proof of the recurrence theorem for a system with an (finite) number of degrees of freedom. Then he applies it to the kinetic theory of gases with remarks similar to those of Poincare.

102 Boltzmann concludes his paper [22] with the following remark:

> The Poincare theorem is of course inapplicable to a terrestrial body which we can observe, since such body is not completely isolated: likewise, it is inapplicable to the completely isolated gas treated by the kinetic theory, if one first lets the number of molecules become infinite, and then the quotient of the time between successive collisions and the time of observation [becomes zero].

Who won the battle? Zermelo or Boltzmann? The physicists decided to follow Boltzmann's view, especially since atoms were beyond any doubt shown to exist.

[6] The kinetic theory if the dissipation of energy, PRS of Edinburgh **8**, 325-34 (1874).

Pure mathematicians, however could not accept Boltzmann's argument: a *theorem* may be true or false, but not *probably true*. In other words: either the H-theorem is a true theorem
103 which can be applied to real gases, or it is not a theorem, and then what are we talking about? Thus Zermelo had won, according to pure mathematicians.
On the other hand, it was a Pyrrhic victory.

104 (Physicists find it strange that) Boltzmann talked about infinitesimal sizes and infinite number of molecules per unit volume, whereas he knew that the size of the molecules, though extremely small, is finite and the number of molecules per unit volume, though extremely large, is also finite. The statements are, on the other hand, a precise indication that Boltzmann fully appreciated that any statistical theory must leave room for fluctuations, no matter how small; these fluctuation can disappear and give birth to to a kind of deterministic theory only if we take appropriate limits.

MD checking of the H-theorem is mentioned.[7]

105 At the beginning of the 1970s it was clear what theorem one should try to prove: "If the distribution is initially factorized, then the one-particle distribution function will be *asymptotically with N tending toward infinity and σ going to zero in such a way that $N\sigma^2$ remains finite*, a solution to the Boltzmann equation: in particular the quantity H associated with it will be, in the same limit, a monotonically decreasing function of time."

106 Lanford: for the time of the order of 1/5 of the mean collision time the solution exists: this is quite sufficient, because already 20% of collisions have occurred.

107 The rigorous theory of the Boltzmann equation started in 1933 with a paper by Torsten Carleman, who proved a theorem of global existence and uniqueness for a gas of hard spheres in the so-called space homogenous case under the restrictive assumption that the initial data is isotropic.[8] Grad's approach was completed by Japanese mathematicians.[9] Lions proved stronger unique existence theorem.

108 In view of the fact that we claim validity for the Boltzmann equation in the Boltzmann-Grad limit only, we do not have to worry about the recurrence paradox either.

110 It is sufficient to define as the direction of increasing time that in which entropy increases. This was more or less Boltzmann's suggestion.

The expansion of the universe is thus ultimately related to all physical processes down to the most minute dimension, and a deeper comprehension of the laws of physics could allow us one day to deduce the expansion of the universe from the observation of very small-scale phenomena.

113 As a matter of fact, the H-theorem and the Boltzmann equation itself can be obtained only

[7] B J Alder and T E Wainright, Studies in molecular dynamics II. Behavior of a small number of elastic spheres JCP 33 1439 (1960); A Bellemans and J Orban, Velocity inversion and irreversibility in a dilute gas of hard disks, PL 24A 620 (1967).

[8] Acta Math 60, 91 (1933).

[9] Nishida and Imai, PRIMS 12, 229 (1977), Shizuta and Asano, ProcJAcad 53 3 (1974), Ukai ibid, 179 (1974).

at the cost of restricting the initial values. Why these initial values are suitable for computing the future and not the past can be explained only at the cost of introducing anthropocentric arguments, which may vary from our conceptions about past and future, which sounds like postulating the irreversibility we wish to prove, to the way we handle macroscopic apparatus.

115 We shall skip here a discussion o the still (after the discovery of DNA!) much quotes views of Bergson on time, which lead to thinking that life and matter are two opposed concepts, since the second can be understood by reason, the first (allegedly) only by intuition.

117 One important aim of the philosophy of science should in fact be that of reconciling our intuitive views, arising from everyday life, with the objective findings of scientists. In fact our common views are frequently "illusions" from the viewpoint of scientific laws.

J Bricmont and Prigogine[10] As pointed out by Bricmont, Prigogine, with his brilliant style, writes sentences that may sound appealing to philosophers and laymen (and unfortunately to some scientists as well) but puzzle well-informed scientists. Either his claims are take literally, and then they are wrong; or they are suitably reinterpreted and then they express standard ideas in a confusing way.

118 The technical trick of taking the Boltzmann-Grad limit is useful in order to eliminate fluctuations which may play a role only for extremely small volumes of for times incredibly long and completely beyond the possibilities of human observation.

The new facts discovered in the twentieth century are all favor of Boltzmann's standpoint. We now feel that there must be a connection between the Second Law and the expansion of the universe: Boltzmann was the first to point out, in his second answer to Zermelo, that cosmological arguments were needed to explain the fact that the initial data are a subset of all the conceivable ones.

6. Boltzmann's relation and the statistical interpretation of entropy

120 his statements (= "It has thus been rigorously proved that, whatever may be the initial distribution of kinetic energy, in the course of a very long time it must always necessarily approach the one found by Maxwell."
... his statements are actually true only when, by taking a suitable limit, the statistical fluctuations disappears; furthermore, probability plays a heavy role in excluding certain initial data.

121 Lord Rayleigh wrote: "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 out of the water again."

126 the first mathematician to hit upon the logarithm of a probability was De Moivre.

129 We remark that Boltzmann quotes Burbury's paper[11] as the origin of his assumption of "molecular chaos" in his lecture on gas theory. We also remark that S H Burbury was the

[10] Physicalia Magazine 17 159 (1995); 17, 213 (1995); 17, 219.
[11] Boltzmann's minimum function, N 51 78 (1894).

first to use the letter H in pace of E for what we call the H-theorem, and this choice was adopted by Boltzmann.

7. Boltzmann, Gibbs, and equilibrium statistical mechanics

134 Boltzmann stated statistical mechanics with a basic paper.[12]

Boltzmann called ensembles monode.
The ensembles for which thermodynamics holds (i.e., $(dE + PdV)/T$ becomes an exact form) are called orthodes.
Boltzmann showed at least there are two orthodes: microcanonical (ergode) and canonical (holonde).

135 M J Klein's excellent papers.[13]

He spent a year each at the universities of Paris, Berlin, and Heidelberg, attending a variety of lectures and reading widely in both mathematics and physics. The list of scientists whose lectures he attended is impressive, since it includes Liouville, Darboux, Kronecker, Weierstrass, Helmholtz, and Kirchhoff.

136 His financial independence and his scientific abilities must have been known within th Yale community, since he was appointed to the newly created professor of mathematical physics in 1871 "without salary."

Gibbs's first paper was on thermodynamics and immediately demonstrated his mastery of the field. The choice of the subject show no correlation to the lectures he had attended in Europe. $\cdots$
The title of the paper. "Graphical methods in the thermodynamics of fluids" is not very promising, but its content quietly changed the content of thermodynamics by using entropy as an independent variable, something the not even Clausius had ever done.

137 he sent copies of his papers directly to some 75 scientists at home and abroad. We cannot tell how many of those actually read his first two papers, but we do know of one, the crucial one, Maxwell. he read Gibbs with enthusiasm and profit. In fact, he had misused the term entropy in the first edition of his book, where he had followed his friend Tait. The error was corrected in later editions, after Maxwell had learned the proper definition from Gibbs's papers.

139 Gibbs's memoir had become widely known in Europe and had received the recognition it merited. It was translated into German by Ostwald, into French by le Chatelier.

140 Maxwell wrote:

By the study of Boltzmann I have been unable to understand him. He could not understand me on account of my shortness, and his length was and is an equal stumbling block to me.

[12] Über die Möglichkeit der Begründung einer kinetischen Gastheorie auf anziehende Kräfte allein, Wien Ber 89 714 (1884).

[13] The development of Boltzmann's statistical ideas in *The Boltzmann equation: theory and applications*(Cohen + Thirring 1973); The scientific style of Josiah Willard Gibbs, in *Springs of scientific creativity* (Aris ed University of Minnesota Press 1983).

141 Gallavotti claims that the reason for its obscurity is due rather to the fact that Boltzmann's work is known only through the popularization buy Ehrenfests' encyclopaedia article, which is as good a treatise on the foundation of statistical mechanics as it is in having little to do with many of Boltzmann's key ideas.

142 Gibbs's theory is a branch of rational mechanics, a sort of projection of the latter discipline on to thermodynamics, a projection performed with analogies, the validity of which is discussed by Gibbs himself.

in the introduction he states that only the principles of statistical mechanics could supply the "rational foundation of thermodynamics" and that the laws of the latter discipline were only an "incomplete expression" of these more general principles.

143 Gibbs wrote to Rayleigh:

> Just now I am trying to get ready for publication something on thermodynamics from te point of view, or rather on 'statistical mechanics,' of which the principal interest would be in its application to thermodynamics—in the line therefore of the work of Maxwell and Boltzmann. I do not know that I shall have anything particularly new in substance, but shall be contented if I can so choose my standpoint (as seems to me possible) as to get a simpler view of the subject.

8. The problem of polyatomic molecules

156 Boltzmann suggested that some of the equilibrium states studied in thermodynamics are really only assumed to be equilibrium states, though they are not, because the ties of variation are enormous with respect to our times of observation.

9. Boltzmann's contribution to other branches of physics

165

> The concepts of differential and integral calculus divorced from any atomist notions are typically metaphysical, $\cdots$

166 Boltzmann's two-volume classical mechanics: In the first volume we find a conceptual contribution by Boltzmann concerning the definition of distinguishability of particles.
The first axiom of classical mechanics laid down by Boltzmann states: identical material particles which cannot occupy the same pint of space at the same time can be distinguished by their initial conditions and by the continuity of their motion.

10. Boltzmann as a philosopher

171 Realist: a realist is somebody who believes that the world outside us exists independently of our sensation, observations, and consciousness, and the human mind can construct an image of this world with the help of sensations and more of less accurate experiments in such a way that the objective image does not explicitly contain our sensations, but can explain all of them.
Metaphysics: scientists in general and Boltzmann in particular have in mind Kant's definition in his "Prolegomena":

> First, as concerns the sources of metaphysical cognition, its very concept implies they cannot be empirical.

Its principles (including not only its maxims but its basic notions) must never be derived from experience. It must not be physical but metaphysical knowledge, viz., knowledge beyond experience.

173 Boltzmann writes:

One does indeed hear occasionally doubts whether insects or divisible animals like certain worms have sensations, but a sharp boundary where sensing stops cannot be given.

174 Boltzmann's summary of Mach's point of view:

Mach pointed out that we are given only the law-like course of our impressions and ideas, whereas all physical magnitudes, atoms, molecules, forces, energies, and so on are mere concepts for the economical representation and illustration of these law-like relations of our impression from sensation.

175 Even the success of theoretical physics is explained on evolutionistic grounds, as one can read in "On the question of the objective existence of processes in inanimate nature":

The brain we view as the apparatus or organ fro producing world pictures, an organ which because of pictures' great utility for the preservation of the species has, conformably with Darwin's theory, developed in man to a degree of particular perfection, just as the neck in the giraffe and the bill in the stork have developed to an unusual length.

176 In January 1905 Boltzmann delivered a speech at the Vienna Philosophical Society originally bearing the title"Proof that Schopenhauer is a stupid, ignorant philosophaster, scribbling nonsense and dispensing hollow verbiage that fundamentally and forever rots people;s brains". This title sounds a bit harsh and as such it was refused , to be come simply, "On a thesis of Schopenhauer's", but in the written text of his conference Boltzmann indicates that he had originally given the former title and explains that he had taken it from a paper by Schopenhauer himself, just changing the name of the philosopher to whom it referred (and who, though Boltzmann does not say this, was Hegel).

In this conference, the thoughts of all philosophers, Kant included (although Boltzmann somehow respected him), are declared to be fundamentally unsound. His aim, he claims, is the liberation of mankind from that mental headache which is called metaphysics.

In this text Boltzmann explicitly calls his own philosophy "materialism," which he says: " Idealism asserts that only the ego exists, the various ideas, and seeds to explain matter from them. Materialism starts from the existence of matter and seeks to explain sensations from it."

177 "What then will be the position of the so-called laws of thought in logic?" Boltzmann asks himself. His answer is immediate:

Well, in the light of Darwin's theory, they will be nothing else but inherited habits of thought.

Endeavor towards acting in an advantageous way has perfected these ideas to produce a world of will and representations. "Even Schopenhauer could not wish better," adds Boltzmann, ironically.

178 In St Louis Boltzmann preceded i=his updated survey of statistical mechanics with a discussion on why physicists are interested in questions that were once left to philosophers:

179 These laws of thought have evolved according to the same laws of evolution as the optical apparatus of the

eye, the acoustic machinery of the ear and the pumping device of the heart.

...We cannot claim that these organs are absolutely perfect. Boltzmann draws the conclusion that "just as little must the laws of thought be taken as absolutely infallible." They have just evolved to the point of grasping what is necessary for life and practically useful.

It is thus not surprising if the forms of thought that have become habitual are not "quite adapted to the abstract problems of philosophy which are so far removed from what is applicable in practice, nor have yet become so from Thales till now."

180 Boltzmann recognizes that our innate laws of thought are indeed the prerequisite for complex experience, but they were not so foe the simplest living beings. Evolution started there, however; the laws of thought developed slowly, but simple experiences were enough to generate them.

181 Boltzmann also thought ethics in terms of evolution.

Notice that Boltzmann mentions 'the so-called Brownian molecular motion, happens with all small particles as is well known".[14]

182 (in the same Schriften)Does there not sound louder than ever then whimper of all obscurantists, the enemy of free thinkers and of enquiry, against the new Pythagoras theorem, Darwin's teaching? ... But, lucky us! It is the thunderstorm that forecasts the arrival of spring. Until then, however, light-hearted pleasantries are premature; arm yourselves for a bitter, bloody struggle.

183 Nobel laureate Odhysseas Elytis"...as the sun rises, the guns of all the great world theories are silenced....."

It is certainly true that only a madman will deny God's existence, but is equally the case that ll our ideas of God are mere inadequate anthropomorphisms, so that what we thus imagine as God does not exist in the way we imagine it. If therefore one person says that he is convinced that God exists and another that he does not believe in God, in so saying both may well think the same thoughts without even suspecting it.

184 when we form quite novel ideas, such as those of space, time, atoms, the soul, or even God, odes one know, so I asked myself, what is meant by asking whether these things exist? Is not the only correct thing to do here to try to clarify what concepts one is linking with the question as to the existence of these things?

185 Boltzmann analogizes Maxwell's calculation of transport coefficients with Leverrier's prediction of Neptune.

Another paper which plays an essential role in grasping how Boltzmann estimated the successes and the difficulties of the atomic hypothesis is entitled, "On the indispensability of atomism in natural science" (1897):

While phenomenology requires separate and mutually rather unconnected pictures for the mechanical motion of centres of gravity and rigid bodies, for elasticity, hydrodynamics and so on, present day atomism is a perfectly apt picture of all mechanical phenomena, and given the closed nature of this domain we can hardly expect it to throw up further phenomena that would fail to fit into that framework.

[14] *Theoretical physics and philosophical problems* a partial English translation of *Populäre Schriften* (Birth, Leipzig 1905).

186 Phenomenology believed that it could represent nature without in any way going beyond experience, but I think this is an illusion. No equation represents any process represents any process with absolute accuracy, but always idealizes them, emphasizing common features and neglecting what is different and thus going beyond experience.

187 Boltzmann is of the opinion that the task of theory consists in constructing a picture of the external world that exists purely internally and must be our “guiding star”.

189 Boltzmann anticipated the view Thomas Kuhn on scientific revolution, can be grasped from the following passage in an obituary for Joseph Stefan (1895):

The layman may imagine the new notions and causes of phenomena are gradually added to the existing basic ones and that in this way our knowledge of nature undergoes a continuous development. This view, however, is erroneous, and the development of theoretical physics has always been by leaps. In many cases it took decades or more than a century to fully articulate a theory such that a clear picture of a certain class of phenomena was accomplished. But eventually new phenomena were discovered which were incompatible with the theory; in vain was the attempt to assimilate the former to the latter. A struggle developed between the followers of the theory and the advocates of an entirely new conception until, eventually, the latter was generally accepted. Formerly one used to say that the old view had been recognized as false. This sounds as if the new ideas were absolutely true and, on the other hand, the old (being false) had been entirely useless. Nowadays, to avoid confusion in this respect, one just say: the new way of idea is a better, a more complete and adequate description of the facts. Thus the following are clearly expressed: (1) the earlier theory, too, had been useful because it gave a true, though partial, picture of the facts; (2) the possibility is not excluded that the new theory in turn will be superseded by a more fitting one.

190 As a matter of fact, a surprising but undeniable aspect of the contributions of Boltzmann to philosophy lies in the fact that they seem to have remained unknown to most philosophers of the twentieth century.

191 Boltzmann’s education in philosophy: he was no autodidact, Gymnasium in Linz and U Vienna curricula had philosophy courses.

192 We can perhaps agree, in a Solomonic way, with both Broda and Wilson. Boltzmann had an exceptional preparation in philosophy, compared with a physicist of today (especially if young and/or American), but certainly at a level that was not impossible to find in the *Mitteleuropa* of his days, and as such he is to be considered an autodidact. We recall, by way of analogy, that Faraday was essentially an autodidact in physics!

194 de Regt finds that both men’s views are realist, mechanist, and materialist, but indicates that the fundamental difference between them lies in the fact that theory came first and empirical reality was only secondary for Boltzmann, whereas the opposite order must be applied to Maxwell’s scientific view.

According to de Regt, the issue (of realism) can be resolved by carefully distinguishing between three levels (ontological, epistemological, methodological) at which one can talk of realism. There is no doubt that Boltzmann is a realist at the ontological level.

The question of the interpretation of theories is of epistemological nature. What can be known about unobservable reality? ...de Regt proposes to call his position *constructive re-*

alism. this realism should not prevent us from accepting freely created models for reality, even more than one at the same time.

195 In fact, when we come to the methodological level, Boltzmann, contrary to Maxwell, argues that the empirical world is so complex that one would not go very far if one made it the starting point of scientific work. Several theories can exist at the same time and can be appropriate for different purposes.

196 Boltzmann was a passionate advocate of the objective existence of the real world, to the point of considering the possibility of changing the rules of our logic if they do not conform to our experimental findings.

197 his passionate reference to Darwin's theory of evolution as a foundation for philosophy is the touchstone for his realism.

11. Boltzmann and his contemporaries

198 Summary: Stefan introduced him to Maxwell's papers.
Boltzmann took leaves of absence to work with Bunsen and Königsberger in Heidelberg, and with Kirchhoff and Helmoholtz in Berlin.
Friendship with Loschmidt
Contacts with Lorentz, Helmholtz, Rayleigh, Ostwald, his colleagues in Munchen (van Dyck, Pringsheim, Lommel, Sohnke, Nayer, Seeliger, Linde)., Brentano
Students: Ehrenfest, Hasenöhrl, Mayer, Meitner, Arrhenius, Nernst.

There is more than enough to belie the idea of a Boltzmann isolated from the science of his days. Yet it is fact that his scientific position appears to be rather singular and almost isolated in the framework of the scientific research of his century.

199 Maxwell's kinetic theory: the method of transfer equation in 1866.[15]

200 There is a singular circumstance in the relation between Maxwell and Boltzmann. The former never mentions the H-theorem.
Boltzmann derived the equipartition theorem, on which Maxwell wrote a paper which rederived the Maxwellian using S_N.[16]

202 As to Lorentz: Boltzmann wrote (Dec 21, 1890): "From the stamp and the handwriting, I recognized that the letter came from You and I has a moment of joy. True, every letter of Yours means that I made a mistake; but I lean so much on these occasions that I would even like to make more mistakes, in order to receive more letters from You."

203 The supporters of so-called "energetics" considered Leibniz as their founding father.

209 After Perrin, Ostwald completely reversed his views: "I am now convinced that we have recently come into possession of experimental proof of the discrete of grainy nature of mat-

[15] On the dynamical theory of gases, PTRS 157, 49-88 (1867).

[16] On Boltzmann's theorem of the average distribution of energy in a system of material points, Trans Cambridge Phil Soc 12, 90-3 (1879).

ter, for which the atomic hypothesis had vainly sought for centuries, even millennia."

However, Mach was, as Brush says, the unrepentant sinner.

210 Until, like St Paul on the road to Damascus, he was dazzled by the revelation which appeared to him precisely during his study of black-body radiation, in the form of Boltzmann's statistical methods, Planck's position was that of a convinced follower of Mach's philosophy, as he earnestly admitted.[17]

Planck wrote: In the eighties and nineties of the last century, personal experience taught me how much it cost a researcher who had had an idea on which he had reflected at length to try to propagate it. He had to realize how little weight the best arguments he exhibited to that end carried, since his voice had not sufficient authority to impose it on the world of science. In those days it was a vain enterprise to try to oppose such men as Wilhelm Ostwald, Georg Helm, Ernst Mach.[18]

211 Nernst continues Boltzmann's ideas in philosophy of science, in particular the idea usually attributed to Kuhn.

12. The influence of Boltzmann's ideas on the science and technology of the twentieth century

214 On Brownian motion: "...likewise it is observed that very small particles in a gas execute motions which result from the fact that the pressure on the surface of the particles may fluctuate."

215 After the initial excitement, interest in Brownian motion disappeared for about thirty years. When the kinetic theory of gases reached a certain stage of development, a connection with molecular motion was suggested. However, Clausius, Maxwell, and Boltzmann are conspicuous by their absence from the debate.

The idea of a connection between Brownian motion and molecular motions began to appear in several papers, but nobody attempted a calculation. In 1879 the German botanist Karl Nägeli attempted to disprove this connection, essentially by noting the enormous difference in size between a molecule and a Brownian particle, which would result in movements much slower than those actually observed. The same kind of argument was independently used by the British chemist William Ramsay in 1882. Then people started to invoke coordinated movements, among them the French physicist Léon Gouy, who pointed out that in any case, Brownian motion would violate the Second Law.

Einstein himself mentioned his own astonishment at the fact that this result had not been obtained by Boltzmann, saying in a conversation that "it is puzzling that Boltzmann did not himself draw this most perspicuous consequence, since Boltzmann had laid the foundations for the whole subject."[19]

221 Boltzmann proved Dulong-Petit's law.

[17] Zur Mach's Theorie der physikalischen Erkenntniss. Eine Erdiderung. Phys Z 11, 1186 (1909).

[18] *Ursprung und Auswirkung wissenschaftlichen Ideen* (Berlin, 1933)

[19] to Sommerfeld, Phys Z 18 533 (1917).

222 Einstein's work is remarkable because it was the first in which quantum statistical concepts were applied to something different from thermal radiation.

Why did people before Einstein miss the opportunity to develop his theory? Because they underestimate the role of fluctuation.

224 An exact solution to the Boltzmann equation.[20]

226 **Epilogue**

Here we simply quote the comment of this grandson D. Flamm:[21] During a vacation in Duino, near Trieste, my mother, Elsa Boltzmann, of whom her father used to say that she was the sunshine of his life, found her father hanged. She was only fifteen years old.

[20] C Truesdell, On the pressure and the flux of energy in a gas according to Maxwell's kinetic theory. II., J Rational Mech Anal 5 55 (1956).

[21] D Flamm, Ludwig Boltzmann and his influence on science, Studies in History and Philosophy of Science, 14, 255 (1983).