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Boltzmann and the Heuristics of Representation in Statistical Mechanics

Cássio C. Laranjeiras;[1] Jojomar Lucena;[2] José R. N. Chiappin[3]

Abstract:

Boltzmann's work in physics has been studied almost always opposing a strictly mechanical approach of the 2nd law of thermodynamics – attributed to his first works in kinetic – molecular gas theory (1866-1871) – to a probabilistic approach, built and developed in his later works (1872-1884). The analysis of the use of these different approaches covers a spectrum of positions ranging from the recognition of an intrinsic incoherence to Boltzmann's thinking, go through a radical change in the development of his work, until the adoption of pluralistic strategies as justifications for their methodological options. The purpose of this paper is to explore Boltzmann's research program from the view of what we characterize as *heuristics of representation,* highlighting the tools used he used for the solution of problems related to thermal phenomena. We will argue that what in the standard historiographical analysis is understood as a radical turn in Boltzmann's work – probabilistic "turn point", that is, the use of an overtly statistical terminology (combinatorial formalism, 1877) instead of a kinetic language (kinetic formalism, 1872) in the analysis of evolution toward the thermal equilibrium (Maxwell's distribution) – could be better understood as a change of representation within the same conceptual framework.

Keywords: Boltzmann; Statistical Mechanics; Heuristics of Representation

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Introduction

The second half of the 19th century witnessed – to use a concept from Lakatos' epistemology

[1] Cássio C. Laranjeiras [Orcid: 0000-0003-4158-8077] is a Professor of Physics in the Institute of Physics at the University of Brasilia – UnB. Address: Campus Universitário Darcy Ribeiro – Asa Norte, Brasília – DF, 70919-970, Brazil. E-mail: cassio@unb.br
[2] Jojomar Lucena [Orcid: 0000-0001-6097-0066] is a Researcher in the Department of Economics at the University of São Paulo – FEA – USP. Address: Av. Prof. Luciano Gualberto, 908 – Butantã, São Paulo – SP, 05.508-010, Brazil. E-mail: jojomarls@gmail.com
[3] José R. N. Chiappin [Orcid: 0000-0003-3202-2274] is a Professor of Economics in the Department of Economics at the University of São Paulo – FEA – USP. Address: Av. Prof. Luciano Gualberto, 908 – Butantã, São Paulo – SP, 05.508-010, Brazil. E-mail: chiappin@usp.br

– the *degeneration*[4] of the *mechanistic program.*[5] The status of the mechanical view of the world, established through the immense philosophical influence reached by Newtonian mechanics, the great finished scientific theory of its time, had come under suspicion for several reasons, including the autonomy achieved by thermodynamics through the works of W. Thomson (1824-1907) – the later Lord Kelvin – and R. Clausius (1822-1888) and the development of the Maxwell – Faraday theory of electromagnetism carried out by Heinrich Hertz (1857-1894). At the end of this same century, alternatives to the mechanistic program were being proposed and passionately debated, with the *energetics program* proposed by Pierre Duhem (1861-1916) deserving special mention, a program that aspired to a broad unification of physics based on thermodynamics, more specifically upon the energy concept.[6] For a discussion on the energetics movement, which focuses particularly on the works of Georg Helm, Willard Gibbs, Wilhelm Ostwald, and Ernst Mach, among others, see (Deltete 1983).

Ludwig Boltzmann (1844-1906) was a remarkable presence in this debate (Deltete 1999, 45-68). As a great advocate of the twin banners of mechanism and atomism (Lindley 2001), he developed a rich and complex *research program*, specifically in the kinetic – molecular theory of gases.[7] Through its advancement, it was possible not only to formulate a brilliant defense of the mechanistic program, although modified, but also to develop an introduction to the theory of probabilities as a fundamental law of physics, the 2nd law of thermodynamics, laying the foundations of modern statistical mechanics[8] and even paving the road for quantum theory (Flamm 1997). Besides, he wrote extensively on philosophical issues, especially about the philosophy of science, although his systematic interest in this matter emerged only after he had given his important contributions to physics,[9] which makes

[4] The term *degeneration* was used by philosopher of science Imre Lakatos (1922 – 1974) to represent the stage through which *Research Programs* pass when they no longer can achieve the expected success in resolving the proposed problems. The model of *Research Programmes* was formulated in an attempt to resolve the perceived conflict between different views of dynamics of construct of science, more specifically between K. Popper's falsificationism and the revolutionary structure of science described by T. Kuhn. See (Lakatos 1984, 47-89) and (Kulka 1977, 325-344).

[5] The origins of a mechanical or mechanistic outlook on the world can be found in the physics of the ancient world, although a clear definition of what we might call a mechanistic program dates back to the 17th century, with such names as Galileo, Boyle, Pascal, Huygens, Descartes and Newton, whose works contributed to its establishment and progress, removing the concept of *final cause* and most of the concepts of Aristotelian *form*, *substance* and *accident* that had dominated medieval thought in natural philosophy (Hankins 1985, 13). In the 19th century the mechanistic insight played an important role in physics. Under the term mechanic or mechanistic, we understand here the mathematical description of nature based on the concepts and methods pertaining to the science of motion, in which all entities are defined in terms of matter, motion, and central forces. See also (Boas 1952, 412-541) and (Strien 2013, 191-205).

[6] The energetics program was very concerned with an epistemological reconstruction of the objective core of knowledge and saw itself as a response to the need for providing a physical interpretation to purely mathematical operations. In this sense, the construction of all concepts and the realization of all calculations should take the amount of energy present in the system as their starting point. An extensive discussion on the research program of P. Duhem can be found in (Chiappin 1989) and (Oswaldo 1998, 79-140).

[7] This theme was the subject of a previous publication (Laranjeiras et al. 2006) made by us when we emphasized Boltzmann`s research program based on the tools and methods used by him in the analysis of thermal phenomena.

[8] From a modern perspective, we could say that statistical mechanics is a formalism that seeks to objectively explain the physical properties of a very large quantity of matter based on the dynamic behaviour of its microscopic constituents (Pathria 1972).

[9] His scientific papers, collected in *Wissenschaftliche Abhandlungen*, contain more than 100 papers on statistical physics alone. See (Boltzmann 1909).

his trajectory particularly interesting, in so far as his philosophical reflections reflect and systematize his scientific experience.[10]

Boltzmann's work in physics has been studied almost always opposing a strict mechanical approach of the 2nd law of thermodynamics – attributed to his first works in kinetic theory of gases (1866-1871) – to a probabilistic approach, built and developed in his later works (1872-1884) (Klein 1973, 53 – 106; Brush 1976, 603 – 630; Brush 1986; Elkana 1974, 243 – 279; Uffink 2007, 2017). The analysis of the use of these different approaches covers a spectrum of positions ranging from the recognition of an intrinsic incoherence to Boltzmann's thinking (Uffink 2017), go through a radical change in the development of his work (Klein 1973 53-106; Brush 1976, 603-630; Brush 1986), until the adoption of pluralistic strategies (Badino 2011, 353-378) as justifications for their methodological options.

Badino identifies the birth of this standard historiographical reconstruction "with the publication of Klein's paper, The Development of Boltzmann's Statistical Ideas" (1973) (Klein 1973, 53-106), where he clearly advocates a radical turn in Boltzmann's views, especially with respect to the introduction and the meaning of probability from 1868 to 1877 (Badino 2006).

Defending the use of pluralistic strategies by Boltzmann and adopting a continuity line in contrast to the idea of rupture in his work, Badino argues that his theory of equilibrium states, developed in the initial period (1868-1871), depends on foundations that are both mechanical and probabilistic and that the non – equilibrium theory (1872-1877) stems directly as a development of these foundations (Badino 2006). Moreover, he shows that the extensive use of asymptotic conditions allowed Boltzmann to bracket the problem of exceptions of the H–theorem[11] (Badino 2011, 353-378).

By adopting a similar perspective and assuming the independence of Thermodynamics in relation to Mechanics in Boltzmann's thought, Aurani defends the idea that probability already appears (although not formally) in Boltzmann's reasoning in his paper of 1866, when treating the irregularity of the movement of atoms in the construction of temperature definition. According to Aurani, as early as 1866, Boltzmann conducted his work in the direction of a probabilistic interpretation of the 2nd law and the concept of entropy insofar as it sought meaning for the mean variations of the mechanical magnitudes of the system, relating them to the motion of an atom (Aurani 1992, 10-63). This reinforces the idea of coherence and no – rupture in the development of Boltzmann's thought.

In support of these ideas, the purpose of this paper is to explore Boltzmann's research program from the view of what we characterize as a *heuristics of representation*, highlighting the tools and methods he used for the solution of problems related to thermal phenomena.[12] The Boltzmann's program was rooted in the context of the mechanistic program of the 19th century and developed coherently and consistently committed to expanding and putting into operation the resources of Mechanics – taken by him as an adequate and unifying representation of the phenomena of nature – in the understanding of the 2nd law of thermodynamics. In this direction, his initial representation for entropy – associated with Hamilton's minimal action principle – will converge to a mechanical – statistical representation, incorporating new heuristic elements into its research program such as notions of *ensemble* and *probability spaces*. So, if there is a turning point in Boltzmann's

[10] Boltzmann was driven to philosophical reflection by the need to establish a dialog between science and philosophy, without giving up on the specificity of each field, recognizing, but acknowledging a common area of interaction where both fields could talk communicate (Videira 2000, 200; Broda 1983, 97).

[11] The understanding of the non – admission of exceptions to the H–theorem by Boltzmann in his paper of 1872 lies at the heart of the argument in defence of a statistical turn in his thinking from 1876.

[12] A detailed discussion of the heuristic of representation in science taking the physics of Descartes and Fermat as an example can be found in (Laranjeiras et al. 2017).

thought we should look into his representational transition and not into his probabilistic approach.

The paper is organized as follows: in sections 2 and 3 we will briefly present, from a heuristic point of view, Boltzmann's representational perspective on scientific theories and his insertion in the context of the mechanistic program of the 19th century. Sections 4, 5 and 6 are devoted to showing how Boltzmann made use of the heuristics of representation in the development of statistical mechanics. Finally, in Section 7, we address the critiques of H–Theorem and its role in the consolidation of statistical representation in Boltzmann's work.

Boltzmann and the Heuristics of Representation

The idea of representation in science has been the subject of study by different authors (Hughes 1977, 325-336; Suarez 1999, 75-83; 2010, 91 – 101; Van Fraassen 1980, 2004, 794-804), with particular focus on the central role occupied by models in the scientific endeavor (MNT 1999). In the specific case of Boltzmann, his understanding of scientific knowledge and his view of physical theories ("*Bildtheorie*") have been widely discussed in the literature, especially the works of Hiebert (Hiebert 1981, 175-198), Miller (Miller 1984), Wilson (Wilson 1989, 245 – 263), D'Agostino (D'Agostino 1990, 380-398), Blackmore (Blackmore) and Regt (Regt 1996, 1999, 113-134). Although in these studies, as it should be, the representational role of theories in Boltzmann's work is contemplated, we identified an analysis gap related to the heuristic aspect of the representations used by him. As an example, we will argue that what in the standard historiographical analysis is understood as a radical turn in Boltzmann's work – probabilistic "turn point" (Klein 1973, 53-106; BMU 2009, 174-191), that is, the use of an overtly statistical terminology (combinatorial formalism, 1877) instead of a kinetic language (kinetic formalism, 1872) in the analysis of evolution toward the thermal equilibrium (Maxwell's distribution) – could be better understood as a change of representation within the same conceptual framework.

Recognizing Jan von Plato (Plato 1982, 72-89) as one the first to claim that Boltzmann might have envisioned a statistical meaning of the H–theorem from the very beginning, Badino assumes a contrary position of a probabilistic turn on Boltzmann's work, attributing it to what he characterizes as "mechanistic–slumber narrative" (Badino 2011, 353-378). In this direction, his work shows that Boltzmann adopted a pluralistic strategy based on the interplay between a kinetic and a combinatorial approach, which reinforces the idea that these different representations are part of the same frame of reference.

Assuming a position contrary to the idea of a probabilistic turn in Boltzmann's work and assigning it to what he characterizes as a "mechanistic–slumber narrative", Badino brings together important elements that reinforce the idea that these different representations are part of the same frame of reference. The reconstruction of Badino shows that Boltzmann adopted a pluralistic strategy based on the interplay between a kinetic and a combinatorial approach (Badino 2011, 353-378).

The hard core of Boltzmann's philosophical reflection is directly associated with the idea that scientific theories are *representations*, *mental images* of phenomena, committed to the description and understanding of the behavior of nature (Boltzmann 1899a).

Speaking about the meaning of the theories – in reply at a farewell ceremony at Graz (16 July 1890), when had been called to a professorship at Munich – Boltzmann made his vision clear by saying:

> I am of the opinion that the task of the theory consists in constructing a picture of the external world that exists purely internally and must be our guiding star in all thought and experiment; that is in completing, as it were, the thinking process and carrying out

globally what on a small scale occurs within us whenever we form an idea. (Boltzmann 1899a, 33)

According to Boltzmann, science is committed to give explanations of natural phenomena and not merely describe them or predict their occurrence. In this sense, the initial elaboration of images can and should be immediately and constantly perfected, which is the main task of the theory (Boltzmann 1899a).

Boltzmann even considers contradiction as an inherent aspect of the progress of theories, clearly signalling his conception of scientific progress as a consequence of his theoretical pluralism. This perspective is explained by him when he says:

> A closer look at the course followed by developing theory revels for a star that it is by no means as continuous as one might expect, but full of breaks and least apparently not along the shortest logical path. Certain methods often afforded the most handsome results only the other day, and many might well have thought that the development of science to infinity would consist of no more than their constant application. Instead, on the contrary, they suddenly reveal themselves as exhausted and the attempt is made to find other quite disparate methods. In that event, there may develop a struggle between the followers of the old methods and those of the newer ones. The former's point of view will be termed by their opponents out – dated and outworn, while its holders in turn belittle the innovators as corrupters of true classical science. This process incidentally is by no means confined to theoretical physics but seems to recur in the developmental history of all branches of man's intellectual activity. (Boltzmann 1899b, 79)

This perspective will be fundamental so that we can understand the adoption of a statistical representation in the frame of reference of the mechanics adopted by Boltzmann.

Adopting a pluralistic theoretical position devoid of ontological values, which is to say that it cannot ascend to the level of the essences and surpass the plane determined by phenomena, its emphasis rests on the capacity of theories, as representations, to lead to results in correspondence with experience (Videira 2006, 273). In this sense, for Boltzmann:

> (...) it cannot be our task to find an absolutely correct theory but rather ***a picture that is, as simple as possible and that represents phenomena as accurately as possible***. One might even conceive of two quite different theories both equally simple and equally congruent with phenomena, which therefore in spite of their difference are equally correct. The assertion that a given theory is the only correct one can only express our subjective conviction that there could not be another equally simple and fitting image. (Boltzmann 1899b, 91, emphasis added)

From a heuristic point of view, Boltzmann's representational perspective on scientific theories is committed to providing a better picture of phenomena, with no guarantee that this picture is optimal or perfect, but sufficient for immediate goals. Although the content of representations can be objectified, finding referents in reality, representations in themselves do not imply to correspond to reality, but to conform to it. This is clearly reinforced in one of his reflections on the discrete or continuous nature of matter when he says:

> The question of whether matter consists of atoms or is continuous reduces to the much clear one, whether the continuum is able to furnish a better picture of phenomena. (Boltzmann 1899b, 91)

In this sense, his conception of physical theory, together with his "pragmatist and Darwinist roots" – see, e.g. (Regt 1999, 113-114) – , leads us to believe that his understanding was that the atom exists insofar as it has explanatory value, as a theoretical entity derived from a process of elaboration of pictures of reality; ultimately, as a heuristic tool for understanding the world.

The absence of ontological commitments and the emphasis on methods and techniques committed to the solution of problems related to thermal phenomena will be the core of what we are characterizing here as a heuristic of representation in Boltzmann's thought, and which will substantially mark his work in statistical mechanics.

Boltzmann in the Context of the Mechanistic Program

Throughout the 19th century, two great research programs set in the same scenario molded by a broader program – the mechanistic program – were faced with the problems posed by thermal phenomena. On the one hand, a theory of heat developed in the framework of phenomenological thermodynamics, based on general empiric allows and completely independent of statements concerning the ultimate nature of matter. On the other hand, a kinetic – molecular theory, whose foundation focused on statements about the atomic nature of matter and which conceived heat as a form of motion associated with the molecules of substances. Peter Clark, following the model of "scientific research programs" of Imre Lakatos, characterizes these approaches as two major research programs, namely the thermodynamic program and the atomic – kinetic program (Clark 1974, 41). Each possessed a distinct hard core and employed quite different basic principles and heuristic techniques (Clark 1974, 43).

The perspective of the thermodynamic program was the consideration of the existence of a definite relationship between an amount of heat and the work that can be produced by it through any path. From this perspective, the laws of heat should be deducted from these relations. In the middle of the 19th century, the works by Carnot, Kelvin and some preliminary studies by Clausius, to cite a few examples, converged in this direction. The kinetic – molecular program, on the other hand, was based on the assumption that the behavior and the nature of substances resulted from the movement of an enormous amount of elements, which ultimately were ruled by the laws of mechanics. Krönig, Clausius, Maxwell and Boltzmann are representatives of this research program. Clark defends the thesis of the degeneration of the atomic – kinetic program after 1880 and the progressive character of the thermodynamic program, with a subsequent resumption of that after 1905 with the prediction of the existence and magnitude of Brownian motion (Clark 1974, 43).

In contrast to this position, as indicated in the introduction to this paper, our position goes in the direction of indicating the degeneration of the mechanistic program in its strict sense and not of the atomic – kinetic program itself, since it will find new heuristic elements for its development. It's in the context of confrontation between these two programs that one of the major recurring problems faced by theoretical physics in the 19th century can be placed, which Boltzmann would take as a central problem and starting point for his work, namely, the possibility of formulating a consistent molecular model within the classical Newtonian mechanical framework, from which the observable properties of matter could be calculated. This meant giving an explanation of the laws of thermodynamics in terms of the behavior of systems involving a huge number of molecules. In his efforts to represent and understand the observable properties of matter from a microscopic perspective, Boltzmann was faced with the challenge of defining and representing thermodynamic equilibrium. When trying to explain irreversibility, he was led to the investigation of the molecular properties of thermodynamic states and to develop a general treatise of thermal equilibrium, through which he surpassed the then current approaches in the kinetic theory of gases, developed by Clausius and Maxwell. The use of analytical mechanics' tools – considered by Boltzmann as "the entrance gate through which we step into the vast and imposing edifice of theoretical physics" (Boltzmann 1899, 129-30) – guided by his atomistic perspective on the structure of matter, enabled him to treat microscopic motion mathematically and, subsequently, to construct a statistical approach as a representational heuristic resource to understand relations between mechanic sand thermodynamics within his research program.

A Mechanical Representation of Entropy

The frame of reference for the construction of the Boltzmann's program occurred with the publication of "On the Mechanical Meaning of the Second Law of the Theory of Heat" (Boltzmann 1866), in which he sought to use a kinetic approach to understand the thermodynamic irreversibility in the representational framework of mechanics.

The experience shows us that, in their vast majority, the natural processes observed in the macroscopic scale tend to occur in a single direction, i.e., they are irreversible. Tackling the problem of irreversibility, therefore, meant reconciling the irregular, reversible nature of the motion of the constituent elements of a given system, with the regular, irreversible nature presented by these same systems when viewed from a macroscopic perspective.

The relationship between the 2nd law and the constitution of matter had already been laid out in the Clausius' work, who arrived at the definition of entropy through the concept of "disaggregation" (Clausius 1865), a concept related to the internal arrangement of atoms and which measures the degree in which the molecules of a body are dispersed during the heat generation process. A connection with mechanics could be sought by building functions of the coordinates and momentum of the particles that make up the system, which could represent the thermodynamic quantities (temperature and entropy) and the two modes of energy transfer: heat and work (Klein 2010, 58). In addition, it was necessary to make a mechanical distinction between reversible and irreversible processes, which meant constructing a mechanical representation of thermodynamic equilibrium; in other words, basing thermodynamics on a kinetic theory, making irreversibility emerge naturally from the laws of mechanics (Dahmen 2006, 283). This way one could look for a theorem that related these mechanical functions in the same way they were related in Clausius' thermodynamic work. As such, it would be possible to establish a link between mechanics and thermodynamics. This would be Boltzmann's starting point, which is clearly illustrated in the opening of his paper (1866), in which he opens his discussion on the subject

> For a long time, the identity between the first law of the mechanical theory of heat and the principle of living forces [principle of the conservation of energy] has been known; Compared with this, the second law occupies a particularly exceptional position and in no case has its demonstration been assumed to have been made clearly and directly. The purpose of this paper is to provide a completely general and purely analytic proof of the second law of thermodynamics, in addition to discovering the theorem in mechanics that corresponds to it. (Boltzmann 1866, 9, emphasis added.)

Different interpretations have been made about this proposal from Boltzmann, almost always mediated by the reduction of thermodynamics to mechanics (Klein 2010, Dugas 1950, Aurani 1992). Reduction, in the sense that we employ the word here, is the explanation of a theory or a set of experimental laws established in a field of research by another theory that was usually, although not always, formulated in another field (Nagel 1961, 338).

Klein states that Boltzmann's goal was to derive the 2nd law as a "purely mechanical theorem" (Klein 2010, 58). In his view, Boltzmann's insertion into the mechanistic program occurs from the perspective of reduction of the phenomena of nature to mechanics. Dugas points out another perspective which, although related to the latter, relativizes some of its aspects by assuming that Boltzmann intended simply "to give to this principle (2nd law), within the framework of kinetic theory, a purely analytical demonstration, and to find the mechanical theorem which corresponded to it" (Dugas 1950, 153). Therefore, in Dugas's view, Boltzmann's project still assumes some dependence of thermodynamics on mechanics, the latter being in the position of reference to the former. Aurani, concerned with a possible reductionist identification of Boltzmann's thought with the mechanistic, defends the idea that he did not seek the reduction of the 2nd law to a mechanics theorem, through a proof of its theoretical nature, nor to translate it into a framework of kinetic theory. She assumes the independence of Thermodynamics in relation to Mechanics in the thought of Boltzmann, who, according to her, sought to make explicit the fundamental character of the law using it as a "guide in the formal treatment of the irregular variation of the mechanical magnitudes of the system and the establishment of coherence between the visible stability of the macroscopic bodies and their continuous variation at the microscopic level" (Aurani 1992, 12).

We are faced with three positions that are not at all irreconcilable and which, therefore, can translate different elements of Boltzmann's program. Our thesis is that Boltzmann's program is inserted in the context of the mechanistic program of the nineteenth century committed to putting into operation the resources of mechanics to give a proper and unified representation of Nature. The operability of these resources in solving problems within heat theory had already been expressed in the kinetic theory of gases and it was, therefore, necessary to extend their possibilities, especially of analytical mechanics, now in dealing with the problem of the thermodynamic irreversibility. In this sense, the idea of reduction thermodynamics to mechanics minimizes the complexity and dynamics of Boltzmann's thought.

Making use of a definition of temperature inspired by kinetic theory – working with the temporal mean of the kinetic energy of atoms – Boltzmann would seek to establish relationships between the 2nd Law, in the form established by Clausius, and Hamilton's principle of least action. His strategy was therefore to use the formalism of mechanics to represent the relationships between the changes in state of bodies and the variation of action in the motion of atoms. As such, he formally established the relations between the quantity of heat supplied to the bodies and the variation of in motion of each atom in space – through the equality between the variation of the action and the variation of the kinetic energy of each atom – with the following expression:[13]

$$S = \iint \frac{\delta Q}{T} dk = 2 \sum log \int_{t_1}^{t_2} \frac{mc^2}{2} dt + C \qquad (1)$$

Although he achieved a mechanic analogy for entropy through the proof of a theorem known as the generalized form of the principle of least action, the explanation for its irreversible increase remained open. In his mechanical characterization of the state of equilibrium, and the consequent mechanical representation of entropy, here stricted himself to strictly periodic, and therefore mechanically reversible, systems. His mechanical counterpart for entropy, given by Eq. 1, was restricted to systems whose molecular configuration repeated after a certain period of time $\tau = (t_2 - t_1)$.

His attempt to extend his proof to non – periodical systems, those where the orbits of particles are not closed, proved unconvincing (Klein 1970, 88), which led him to conclude only that "if the orbits are not closed in a finite time, we can still look at them as closed in an

[13] Boltzmann used the letter "c" (from Latin "celeritas") to indicate speed, as was common at that time.

infinite time" (Boltzmann 1866, 30). Despite this consideration, he was not able to establish a molecular basis for irreversible processes and therefore failed to solve the problem of irreversibility.

Five years later (1871), in On the Reduction of the Second Law of the Mechanical Theory of Heat to General Mechanical Principles (Clausius 1870), Clausius arrived at the same theorem, only this time emphasizing one element ignored by Boltzmann, namely the possibility that the force function (potential energy unction) could be subject to change. According to Daub, this aspect is of utmost importance, since it is only when the force function is considered that the important issue emerges of linking its variation with work (Daub 1969). Afterwards, the potential energy function would be considered by Boltzmann in his new attempt to interpret thermodynamic irreversibility, which he laid out in "Analytical Proof of the Second Law of Thermodynamics from the Law of Equilibrium Distribution of Kinetic Energy" (Boltzmann 1871).

The Distribution Function and the Foundations for a Statistical Representation of Entropy

The construction of a statistical representation as an alternative to a kinetic representation (more strictly mechanical), developed in 1866, was only possible by recognizing the role of Maxwell's molecular speed distribution function – of which Boltzmann would make different interpretations in his papers of 1871 (Boltzmann 1871a, Boltzmann 1871b, Boltzmann 1871c) – allowing him to build new heuristic tools, such as the notions of statistical ensemble and probability of states, which in themselves can be understood as new representations of the states of bodies.

Starting with the same considerations Maxwell made in "On the Dynamical Theory of Gases" (Maxwell 1965), Boltzmann extended the equilibrium distribution to Maxwell's molecular speeds in a monatomic gas, addressing the case when a field of external forces is present, such as the gravitational field (Maxwell – Boltzmann Distribution) (Boltzmann 1868). On his occasion, he presented us with two different methods to achieve this goal: the Kinetic Method and the Combinatorial Method.

Dissatisfied with the derivation of the distribution function developed by Maxwell, which he considered difficult to be understood due to its brief presentation, Boltzmann spent the first section of his paper (1868) filling in some gaps and illustrating some aspects with concrete examples, which, in his understanding, Maxwell had failed to elucidate, such as the nature of the distribution function. It is here that we find for the first time what would become his first definition of the concept of probability (based on kinetic arguments), represented as a temporal average. Probability was identified with the fraction of a sufficiently long time interval, during which the speed of a specific molecule has values within a certain volume in the velocity space. Later (1871), probabilities would appear in a much more explicit way, linked to the concept of the state of a system, defined according to the limits of the coordinates of the atoms.[14]

The combinatorial method is independent of any statements about collisions between the molecules and is not based on any argument of a kinetic nature. Assuming that the probability of finding a molecule in a given region of space is proportional to the "size" of that region, he was able to reconstruct the usual results of thermal equilibrium. Although this method was unsuccessful in deriving the Maxwell distribution in three dimensions, it is

[14] The concept of probability conceived as a temporal average can already be found in the 1866 paper, when Boltzmann treated temperature as a function of the average kinetic energy of each molecule in time (Boltzmann 1866, 14). On that occasion, he made use of probabilistic notions in his reasoning, even though he did not use the word probability.

extremely valuable to the theory of probabilities and to the Statistical Physics (D. Constantini et al. 1997, 486). The central idea behind this method is that the macroscopic description of a state of equilibrium (macrostate) does not distinguish between the many microscopic states (microstates) that are compatible with it. What Boltzmann did was consider a system (a gas made up of a very large, but finite number "n" of molecules) with total energy "E" divided into "k" discrete pieces "x", in such a way that $E = \sum ik_i = nx$, where k_i is the energy of the ith molecule. In general terms, the problem faced by Boltzmann was how to calculate the probability that the energy of a molecule would lie between k and k+dk regardless of the energies of other molecules in the system. His intention was to derive an expression for the number of different possible paths to divide the total amount of energy between the different molecules. His starting point in the search for a solution to the problem was to divide the total energy "nx" of the system in "p" equal parts, so that the continuum of energy values for each one of the molecules were divided into a finite number of intervals This eminently finitist attitude by Boltzmann has always been in agreement with his physical intuition. This outlook would be picked up again in his 1872 paper, when he built an interesting method of work based on the discretization of energy.[15] This procedure was in line with the link of energy that he had defined earlier, i.e. $E = \sum_i k_i = nx$.

By exemplifying this procedure in the case of a system composed of two and three molecules, Boltzmann presented us with a second conception of the notion of probability, designed now as the ratio between the number of favourable cases and the number of possible cases, i.e., the probability that a given molecule would have energy "$k_i x$" is defined as the number of microstates for which the particle "i" has this amount of energy divided by the total number of microstates.[16] This is the so-called particle ensemble average.

Using the equiprobability of states as heuristic argument, Boltzmann made clear why a system in equilibrium should obey Maxwell's law of distribution. Simply because it is the most likely to be found in thermal equilibrium, since it corresponds to the largest number of microstates. Through the work of Gibbs, the hypothesis of equality of probabilities, a uniform distribution of probabilities in the space of states, later led us to the definition of the microcanonical ensemble, a set of microscopic states characterized by a same constant value of energy, which are associated with the same probabilistic weights.

As noted by Klein (Klein 2010, 62) – and as our discussion on kinetic and combinatorial methods also sought to show – Boltzmann interpreted Maxwell's distribution function in two different ways in his analysis of the nature of the thermo – dynamic equilibrium. He seemed to consider them as equivalent, and directly linked to a notion of probability conceived as temporal average and as particle ensemble average, respectively,[17] which came later to be known as ergodic hypothesis. But Boltzmann used the concept of probability to refer to the state of a gas as a whole, which was when he introduced the concept of the probability of a state of a gas. In the third section of his 1868 paper, in which he introduced us to a general solution for the thermal equilibrium problem, his starting point was to consider a system of n material points, representing its coordinates and speed components respectively by x_i, y_i, z_i and u_i, v_i, w_i, where i= 1,2…, n (Boltzmann 1868, 92). By using his first definition of probability as temporal average [originally used in the context of a molecule], he then

[15] This eminently finitist attitude by Boltzmann has always been in agreement with his physical intuition. This outlook would be picked up again in his 1872 paper, when he built an interesting method of work based on the discretization of energy.

[16] The micro states are defined by the designation of k_1 pieces of energy to particle 1, k_2 pieces of energy to particle 2... k_n pieces of energy to particle n, $\sum_i k_i = k_i$.

[17] In the temporal average, probability is identified with the fraction of a sufficiently long time interval, during which the speed of a specific molecule has values within a certain volume in the space of speeds. In the particle ensemble average, it is identified with the fraction of the total number of molecules that, at a given moment, have speeds in a given volume element.

introduced the probability of a certain state of the system as the relative proportion of time in which the gas remains in a given region of space, which was done by indicating the probability that the parameters of the gas take values in certain intervals (Boltzmann 1868, 92-93).

Unlike in 1866, Boltzmann therefore no longer speaks of the trajectory of a particle, but of the limits of the position coordinates and the speed of their set. The probabilities, tested conceptually in the kinetic approach of 1866 and used implicitly in their dual meaning in 1868, would appear explicitly in 1871 through the expression "the probability of different states of bodies" ("die Wahrscheinlichkeit der Verschiedenen Zustände des Körpers"), and are implied in the expression "state distribution" ("Zustandsverteilung"). It is as support of this new representation that "phase space" finds its place as the space of all accessible states to the system under study.

Boltzmann's contact with Maxwell's work, therefore, marked a new stage in the development of his research program, incorporating two new representational heuristic elements:

(1) The use of the "distribution function" to replace a full set of molecular variables;

(2) The replacement of arguments of a kinetic nature, linked to a temporal description of the irregular movement of particles, by arguments of a probabilistic nature, which would establish the relationship between the system's evolution in time and the particles' limits of movement in space.

Based on this new approach, a new method of representation of the thermodynamic equilibrium began to be outlined in Boltzmann's program. It was characterized, on the one hand, by the creation of the statistical ensemble[18] and, consequently, the adoption of a new space that was no longer the μ – space of individual particles, but the space of the entire gas, the Γ – space, called ***phase space***, the space of all states accessible to the system under study;[19] and on the other hand, by there placement of the temporal average by a spatial average, taking over the entire statistical ensemble, in the representation of a given macroscopic physical quantity (thermodynamic variable).

Let's better specify this heuristic level in Boltzmann's thinking, which was built over the year of 1871, at the root of which a hypothesis can be found the Ehrenfests later dubbed the ergodic hypothesis (Boltzmann 1871, 270) (Ehrenfest et al. 1959,21) and which marks his transition from a kinetic approach to statistical approach him a very peculiar way.

To calculate the temporal average of a given quantity A in the laboratory, we usually take the average of its values over a very long period τ. As such, we can write

$$\langle A \rangle_{lab} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} A(t)dt \qquad (2)$$

On the other hand, one could imagine a set of systems distributed in the phase space ("statistical ensemble") in such a way that the density of these systems is given by ρ (q, p). The average value of the quantity A in the ensemble is then given by

[18] This is a set of (fictitious) replicas of the real system, which are similar in their nature (macrostate), but differ among themselves in the particular values that their parameters (position coordinates and momentum) assume at a given moment (microstate). The 'ensembles' were proposed by Boltzmann as a strategy to overcome the difficult problem of keeping track of the temporal evolution of an isolated system made up of many particles (N→∞). Later, the ensemble method became a basic tool of statistical mechanics through the work of Gibbs.

[19] The name μ – Space and Γ – space can be attributed to the Ehrenfests (Ehrenfest et al. 1959).

$$\langle A \rangle_{ensemble} = \frac{\int A(q,p)\rho(q,p)dqdp}{\int \rho(q,p)dqdp} \qquad (3)$$

Boltzmann's hypothesis consisted in assuming that the average values defined by equations 2 and 3 are identical and equal to the thermodynamic value of A. This means assuming that the average of a function in time, obtained by following the points of its trajectory, would be taken on all points and, therefore, would be equal to the phase average.

It is based on this assumption that we will find what the Ehrenfests presented in 1911 as being the "justification of Boltzmann – Maxwell" (Ehrenfest et al. 1959, 21), which became known as the ergodic hypothesis, i.e., the idea that the phase trajectory of a (single) dynamic system is such that it passes in the proximity of all points that are compatible with its total energy.[20]

In Von Plato's view (Plato 1982), admitting to this idea would mean adopting a somewhat careless reading of Boltzmann's work, for whom the idea of a single trajectory filling the entire space of states was not in his horizon. In fact, Boltzmann admits to the possibility of different trajectories (the Lissajous figures are the example of motion he uses), formulating ergodicity as a condition for the existence of only one invariant of motion: total energy. With the impossibility of assigning ergodic behaviour to a single system, which meant admitting the theoretical dependence to initial conditions as possible, Boltzmann would therefore use what he later called a trick (*Kunstgriff*), "the fiction of infinitely congruent independent systems" (Boltzmann 1884, 123), the so – called ensembles, as they became known after Gibbs.[21] For the specific case under consideration here, those where all systems have the same energy, Boltzmann used the expression Ergoden[22] (Gibbs' microcanonical ensemble). This way, the ensembles[23] are introduced as are presentational heuristic resource in the solution of the problem of calculating the macroscopic properties of gases independent from their microscopic evolution. Subsequently, the "ensemble method" became the foundation of statistical physics through the work of Gibbs, who cites Boltzmann in his preface to "Elementary Principles in Statistical Mechanics" (Gibbs 1901, viii) as a pioneer in the use of this type of representation.

To justify this, Boltzmann considered that during the evolution of the system, the time Δt spent in a given element of volume ΔV of the (discrete) phase space is proportional to the volume element, i.e.,

$$\lim_{\tau \to \infty} \frac{\Delta t}{t} = \frac{\Delta V}{V} \qquad (4)$$

where V is the total volume of the region considered.

Suppose that a given system S finds itself, for a sufficiently long period of time τ, in the state S_i for a period of time τ_i. In the same way that we can define the relative frequency of a given event, we can define the relative proportion of time in which the gas remains in that

[20] This position has been the source of controversy, with important contributions from Brush (Brush 1967), von Plato (Plato 1982) and Gallavotti (Gallavotti 1995). Following Brush's reasoning, we would like to highlight here that although the so – called ergodic hypothesis was in Boltzmann's considerations, it was not presented by him as a condition of his theory of gases, as the work by the Ehrenfests (Ehrenfest et al. 1959, 21) would seem to indicate.

[21] We are indebted to Prof. Gallavoti, in (Gallavotti 1995), where for the first time we came across an analysis that clearly established Boltzmann's priority with regard to ensembles.

[22] The term was introduced explicitly for the first time by Boltzmann in 1884 (Boltzmann 1884).

[23] Boltzmann used the term "*Inbegriff von Systeme*" ("the highest representation of the system") to represent them (Boltzmann 1884, 123).

state (τ_i/τ). This was the strategy of Boltzmann when he identified this fraction of time (τ_i/τ) with the *probability of states*.

We can, therefore, understand this period of Boltzmann's work (1868-1871) as marking the beginning of the construction of what is known as Sample Space in statistical language, the space of events, which from a statistical mechanics perspective is the set of all microscopic states (microstates) accessible to the system.[24] In addition, we also recognize Boltzmann's conceptual effort to assign probabilities to the space of states, forging what we now know through the concept of probabilities,[25] the space within which the states will be distributed with their respective probabilities. In this sense, we can see the use of two types of sampling spaces on the horizon of the Boltzmanian program for statistical mechanics, whose unfolding we recognize in Gibbs' work, namely:

(1) **PI Space**: the space where the states are distributed with equal probability and which are represented by the so – called Ergoden from Boltzmann (Gibbs' microcanonical ensemble.)

(2) **PII Space**: the space where the states are divided according to different probabilistic weights, given by the Maxwell–Boltzmann distribution and represented by what Boltzmann called Holode (Gibbs' canonical ensemble.)

We therefore identified a transition in representational heuristics in Boltzmann's program, which goes from a kinetic approach to a statistical approach, using Maxwell's speed distribution function as an element of mediation (C. Laranjeiras et al. 2006). In a statistical language, we can say that in the kinetic approach, Boltzmann attributed the average property of the population (gas) to the sample. In the statistical approach, the distribution function will form the basis of the representation that will allow this extrapolation.

A Mechanical-Statistical Representation of Entropy

The papers of 1871, previously referred to, were without a doubt an important step in Boltzmann's representational transition. Even excluding irreversible phenomena – let us remember that the treatment was exclusively directed to states of equilibrium – Boltzmann was able to develop new tools through this contact with Maxwell's work. His next step was to extend the statistical treatment to irreversible phenomena through a dynamic approach to the process of evolution to thermal equilibrium. This is the emphasis of his 1872 paper, Further Studies on the Thermal Equilibrium of Gas Molecules (Boltzmann 1872), an essay of approximately 100pages presented to the Academy of Vienna.

The paper begins with a critique of the derivation of speed distributions for a gas in thermal equilibrium, given by Maxwell in 1867 (Maxwell 1965), emphasizing the fact that deduction had shown only that the Maxwell distribution, once reached, would not change because of the collisions between molecules. It failed to show, and this was Boltzmann's intention, that the gas should always approach the limit found by Maxwell, whatever its initial state.

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[24] It is within the Boltzmann's program (late 19th century) that we find the framework for the construction of sample spaces in statistical mechanics, which will be perfected, in the sense that they become more operational, by Gibbs (dawn of the 20th century, see (Gibbs 1901)) and will be more thoroughly developed from a mathematical perspective by Kolmogorov in the early decades of the twentieth century. See (Kolmogorov 1950).

[25] This is an important milestone in the birth of statistical mechanics, whose task it would be to build strategies to assign probabilities to the space of states.

In his justification for Maxwell's hypothesis about the statistical distribution of speeds, Boltzmann made use of a dynamic approach[26] by studying the path to equilibrium, i.e., the process by which a given system evolves toward equilibrium. His starting point is based on the collision mechanisms, developed in 1871 (see Boltzmann 1871), that promote the temporal variation of a function [f (v_1,t)] which gives the number of molecules with velocityv1at a given time t1.

By treating collision processes in a precise way, he obtained the time derivative of the molecular distribution function, an integro–differential equation that can be written in the following way:

$$\frac{\partial f(v_1,t)}{\partial t} = \int_0^\infty \int_0^{v_1+v_2} [f(v_1',t)f(v_2',t) - f(v_1,t)f(v_2,t)]\psi(v_1,v_2,v_1')dv_2 dv_1' \qquad (5)$$

This is the so-called Boltzmann's equation, which describes the temporal evolution of f when this function at some initial time is given.

Maxwell had argued that the distribution of velocities will remain stationary if the number of collisions is equal.[27] In Eq. 5 such equality makes the expression in square brackets in integrand vanishes, leading us to the Maxwell distribution. This way Boltzmann showed that the Maxwell distribution is in fact a stationary solution of the equation. But also showed that it is the only one. To prove this he introduced a certain quantity H, a function of the dynamic state of the system which, in the absence of a constant factor, coincides with the entropy of Clausius and which measures how far a system at time t is removed from its state of equilibrium. With this, he ended up proving a theorem, the so – called H–theorem,[28] for the common foundations of the laws of mechanics and the laws of probability, according to which entropy must always increase or remain constant. The H–theorem consists in demonstrating the existence of a certain function, originally represented as E(t) and later as H(t),[29] defined in terms of f (v,t),

$$H(f,t) = \int f(v,t)\ln f(v,t)dv, \qquad (6)$$

where f(v,t) is a solution of Eq. 5, which can never increase, but only decrease or remain constant, i.e.

$$\frac{dH}{dt} \leq 0. \qquad (7)$$

Since H cannot decrease infinitely, it must approach a minimum value and then remain constant, which is the final value corresponding to the Maxwell distribution. Bearing in mind that H is related to thermodynamic entropy in the final state of equilibrium,[30] the result is

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[26] Boltzmann's dynamic approach contrasts with the stationary approach used by Maxwell. In the latter, the starting point is the state of equilibrium right from the beginning, while in the former this state is studied as a result of an evolution process of the system.

[27] Kuhn (Kuhn 1978, 40) notes that Boltzmann made the calculation of the number of collisions that occur in a unit of volume during a time interval dt employing a technique that dates back to Clausius, regarding his calculation of the mean free path of gas molecules. In fact, Boltzmann had calculated the average number of such collisions, although he did not make this aspect explicit. This aspect is of the utmost importance because it characterizes the statistical dimension of Boltzmann's deduction.

[28] A detailed discussion of the H–theorem, including an analysis of the objections around it made by Loschmidt and Zermelo, can be found (Harvey 2009).

[29] Originally Boltzmann called his function E but as this could be confused with E for ENERGY, he changed it to a capital greek letter ETA (=H).

[30] The quantity H is proportional (with a constant of negative proportionality) to the entropy of the gas in the form given by Boltzmann in his 1871 paper (Boltzmann 1871).

equivalent to the proof that entropy must always increase or stay constant. This way Boltzmann established for the first time the fundamental connection between the microscopic approach (which characterizes statistical mechanics) and the macroscopic approach (which characterizes thermodynamics); he even gave us a direct method of calculating the entropy of a given physical system from a purely microscopic point of view. With the H–theorem, Boltzmann tried to explain the irreversibility of natural processes, showing how molecular collisions tend to increase entropy; any initial distribution of molecular positions and speeds will certainly evolve to a state of equilibrium in which the speeds are distributed according to Maxwell's law.

At the end of his paper, after expanding his results to compound gases and polyatomic molecules, affirming that the same methods could be applied to a gas with molecules with complex structures, Boltzmann made the calculation of entropy – establishing a physical sense for the quantity H, which is defined based on the distribution function.

The Criticisms to the H–Theorem and Consolidation of Statistical Representation

The article of 1872 was the target of criticism, which forced Boltzmann to explain the statistical content of his new representation with greater clarity. Formulated in the form of paradoxes – the paradox of reversibility (Loschmidt 1876) and the paradox of recurrence (Zermelo 1896) – the criticisms were specifically related to the nature of the irreversibility in physical systems. The core of the criticisms could be summarized in the following question: How to explain the irreversible behavior of systems from the macroscopic point of view based on mechanical models that are strictly reversible and recurrent? In other words, the issue here was how to reconcile his general equation (Eq. 5) with the classical dynamic.

A contradiction was seen, which Boltzmann sought to dilute, between a basic premise of his derivation, the reversibility of individual collisions, and the irreversibility predicted by his theorem for a system with many particles. From the critics' perspective, it was not possible to reconcile a molecular theory based on Newtonian mechanics and the general principle of dissipation of energy. Boltzmann became aware of the criticism of Loschmidt – his colleague at the University of Vienna and advocate of atomism – through an article presented by him to the Vienna Academy of Sciences in 1876 (Loschmidt 1876).

The response came in 1877 (Boltzmann 1877a), when Boltzmann emphasized the role of probability in his understanding of the 2nd law.

Loschmidt was concerned about some aspects of Boltzmann's work, especially about the possibility of providing a molecular basis for the second law of thermodynamics. Loschmidt's argument, which later became known as the paradox of reversibility, was that we can never derive the irreversible approximation to equilibrium and the monotonic increase of the entropy associated with it from reversible mechanical laws. If entropy is a function specified from the positions and velocities of the particles of a system and if that function increases during some particular movement of the system then by reversing the direction of time in the equations of motion it would be possible to specify a trajectory through which entropy decreases.

In his response to Loschmidt, Boltzmann emphasized that the molecular proof of the 2nd law was not solely based on mechanics, but on mechanics along with the laws of probability. Boltzmann's argument was that although Loschmidt was correct in asserting that reverse motion would produce a decrease in entropy and that this motion was as consistent with the laws of mechanics as the original movement of increasing entropy, he had not attempted to do so that the probability[31] of those initial states which produce an increase in entropy is unusually greater than of those which lead to its diminution. A reversal of this process could not be achieved solely by taking a steady state and reversing molecular speeds. It would be necessary to choose very special microscopic states (in the midst of an immense number of microstates compatible with an equilibrium macrostate) that had been developed from non – equilibrium states. Only the reversal of speed in these cases make it possible to decrease the entropy. But this is quite unlikely.

In a second paper in 1877 (Boltzmann 1877b), the statistical dimension of Boltzmann's thinking becomes more clearly outlined. This paper, where he explicitly states that entropy is a measure of the probability of a state, is the culmination of his studies on the relationship between the 2nd law of thermodynamics and the calculation of probabilities. Over the course of his approach – combining his definition of H (introduced in 1872), the monotonic decrease of H (which emerged as a result of his kinetic equation), the role of entropy (S) in thermodynamics (he had suggested that S is associated with – H), and his concept of the probability of states (W) – Boltzmann wrote for the first time the equation which Planck would later make familiar as $S = K \log W$. The fundamental idea here is that the entropy of a macrostate is determined by the number of ways in which this macrostate can be obtained (microstates) through the different arrangements of the molecules in the system (combinatorial definition of entropy). This is a milestone in Boltzmann's program insofar as entropy, which from the point of view of thermodynamics was given by a trajectory, was now to be related to the number of states accessible to the system.

By emphasizing the role of probability in understanding the irreversibility of the 2nd law, Boltzmann introduced an important method (most likely distribution method) later used by W. Gibbs (1838-1903) in his development of statistical mechanics.

Another criticism came through the so-called "recurrence paradox" (1896), based on a well known theorem from Poincaré, the "recurrence theorem" (Zermelo 1896), according to which a mechanical system contained in a finite volume and with finite energy would, after a finite time, return to the proximity of its initial state. In the hands of Ernest Zermelo (1817-1923), this theorem was used to justify the impossibility of the continuous and monotonic increase of entropy with time. Zermelo showed (Zermelo 1896) that Poincaré's theorem implies that Boltzmann's H–function is an almost periodic function of time and, therefore, that a deterministic mechanical system cannot remain in a final state, as we would expect from the H–theorem. In other words, H(t) decreases during a certain time interval until it reaches its lowest value in the equilibrium and grows back spontaneously to reach its original value, thus contradicting the H–theorem and the second law of thermodynamics.

Boltzmann's reply came in the same year (1896) in an article entitled "Reply to Zermelo's Remarks on the Theory of Heat" (Boltzmann 1896), where he asserts that the 2nd law of thermodynamics was not simply a mechanistic but statistical principle, stating that equilibrium state is not a single configuration of the systems, but a set of possible configurations (majority), characterized by the Maxwell – Boltzmann's distribution. In this sense, the recurrence to some particular initial states would be a mere fluctuation, the occurrence of which would require an infinitely long time. At the beginning of the article he emphasizes very clearly his position:

> Clausius, Maxwell and others have already repeatedly mentioned that the theorems of gas theory have the character of statistical truths. I have often emphasized as clearly as possible that Maxwell's law of the distribution of velocities among gas molecules is by no means a theorem of ordinary mechanics which can be proved from the equations

[31] By probability, Boltzmann was referring to the number of possible paths through which the initial conditions (microstates) could be chosen so that they were compatible with the macroscopic variables observed (macrostates).

> of motion alone; on the contrary, it can only be proved that it has very high probability, and that for a large number of molecules all other states have by comparison such as mall probability that for practical purposes they can be ignored. At the same time I have also emphasized that the second law of thermodynamics is from the molecular viewpoint merely a statistical law. Zermelo's paper shows that my writings have been misunderstood. (Boltzmann 1896, 219)

Throughout the paper, Boltzmann reaffirms the validity of Poincare's theorem denying however that his application by Zermelo to the theory of gases was correct. He recognizes that Zermelo is correct when he states, from the mathematical point of view, the periodicity of the behaviour of the H–function, but emphasizes that this periodicity is far from contradicting his theorem, being in complete harmony with it. Boltzmann admits that recurrence to an initial state is not mathematically impossible, but unlikely.

Conclusions

Throughout this paper, which sought to reconstitute Ludwig Boltzmann's Research Program for Statistical Mechanics from the perspective of representativeness heuristics in science, we highlighted some tools he used for the solution of certain problems related to thermal phenomena. From a mechanical representation of entropy, associated with the principle of least action, passing through the use of Maxwell's distribution function, it was possible to identify the construction (in a coherent and consistent way) of a statistical representation based on the concept of ensemble and the use of probability spaces. In the context of the debates surrounding Boltzmann's work, we defend the idea that if there is a turning point in Boltzmann's thought we should look into his representational transition and not into his probabilistic approach. Here, in our view, is the contribution of the present work, whose historiographical and philosophical perspective – in contrast to the traditional view – allows us to identify representation as a heuristic instrument for articulating its research program.

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