Mechanistic slumber vs. statistical insomnia: The early phase of Boltzmann's H-theorem (1868-1877)

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Abstract

An intricate, long, and occasionally heated debate surrounds Boltzmann's outstanding works on the H-theorem (1872) and the combinatorial interpretation of the second law (1877). After almost a century of devoted and knowledgeable scholarship, opinions are still split on the question whether Boltzmann changed his view of the second law after Loschmidt's 1876 reversibility argument or he already had a probabilistic conception for some years then. This paper argues that there was no abrupt statistical turn in 1877. In the first part of the paper I discuss the development of Boltzmann's research from 1868 to the discovery of the H-theorem. This reconstruction shows that Boltzmann adopted a pluralistic strategy based on the interplay between a kinetic, an ergodic, and a combinatorial approaches. Moreover, it shows that the ample use of asymptotic conditions allowed Boltzmann to bracket the problem of exceptions and fluctuations. In the second part I put forth further arguments to support the claim that Boltzmann was aware of the statistical meaning of the second law before 1876. I also suggest that both Loschmidt's challenge and Boltzmann's response to it did not concern the H-theorem. In effect, the close relation between the theorem and the reversibility argument is a consequence of later investigations on the subject.

Key words: Boltzmann, Statistical Mechanics, H-theorem, Statistical Turn, Ergodic Hypothesis, Reversibility Paradox, Kinetic Theory

1. Introduction: The riddle of the statistical turn

The emergence of statistical mechanics is one of the most consequential conceptual process of nineteenth century. The champion and most eminent campaigner of this process was Ludwig Boltzmann. However, in spite of a plentiful scholarly effort, some key questions concerning Boltzmann's most famous result, the H-theorem, are still far from being settled.

Following the Ehrenfests lead,[1] many working physicists and some historians have supported a narrative according to which, while in 1872 Boltzmann believed the H-

[1] Ehrenfest and Ehrenfest (1911).

theorem to be free of exceptions, he was abruptly awoken from his 'mechanistic slumber' by Loschmidt's 1876 reversibility argument. This criticism made him realize that the H-theorem, as well as the second law, have merely a statistical meaning. Martin Klein has certainly championed this line in Klein (1973), even though in his book on Ehrenfest (Klein, 1970, 94-112) he takes a more prudent stance. Along a similar narrative line, with distinctions that I will mention later on, we find also Kuhn (1978) and, more recently, Uffink (2007) and Brown et al. (2009).

The number of the critics of the 'mechanistic slumber' narrative is not as much large. Jan von Plato has been one of the first to claim that Boltzmann might have envisioned a statistical meaning of the H-theorem from the very beginning,[2] while Michel Janssen has pointed out the role of the authority of the Ehrenfests in making the mechanistic slumber narrative popular among the historians. More particularly, he has suggested that Klein committed a sort of 'creative misreading' by superimposing Ehrenfests's account on his reading of Boltzmann somewhat in the same way as he also superimposed Ehrenfests's account on his reading of Planck.[3] The sticking point is therefore whether Boltzmann's thought has ever experienced a 'statistical turn' between 1872 and 1877. In the next sections I will argue against the mechanistic slumber narrative and the thesis of a statistical turn.

My main argument is a careful reconstruction of Boltzmann's road to the H-theorem. Historiography has tended to take the 1872 paper as a self-contained piece of work, while a look to the complex process which brought it about is overly informative on Boltzmann's attitude towards mechanics and probability. Specifically, it provides us with two indispensable caveats to correctly evaluate Boltzmann's 1872 theory. First, physicists in mid-1800 customarily referred to the gas as a complex systems formed by a collection of molecules in chaotic motion. Properties supposedly stemming from this disordered motion such as the time stability of the averages, the equiprobability of the angles of scattering and so on were massively used. However, there was no attempt to define formally what 'being disordered' means for a mechanical system. Disorder was a feature of gases that was widely *used* to simplify the calculations, but whose understanding remained intuitive.

In addition, people tended to describe disordered systems in a suitable conceptual space defined by assumptions of asymptotic nature: they supposed numbers *sufficiently* large of molecules, time periods *sufficiently* long, volumes *sufficiently* extended, that is assumptions that are fulfilled in ideal conditions. Practically all arguments involving systems with many degrees of freedom explicitly or implicitly deployed these assumptions. Thus asymptotic assumptions often worked as a justification to leave aside many snags concerning fluctuations and exceptions related to pathological microarrangements. I will argue that Boltzmann's apparently deterministic phrasing in 1872 is partly due to the fact that he used disorder intuitively and assumed asymptotic conditions. Boltzmann read the H-

[2] Von Plato (1994).

[3] Janssen (2002). In effect, the historiographical case of Boltzmann resembles closely that of Planck, cf. Darrigol (2001), Badino (2009).

theorem as stating the logical consequences of suitable physical hypotheses laid down in the context of asymptotic assumptions.

Second, after Maxwell's 1867 paper on the equilibrium distribution Boltzmann tried to understand better the concept of equilibrium and the conditions sufficient to attain it. In his 1868 paper he came up with no less than three different ways of getting at Maxwell's distribution: to the classical collisions analysis, he added an ergodic argument, and a novel, purely combinatorial argument (section 2.2). Instead of driving a wedge between these methods, Boltzmann used them alternatively in order to attain a deeper understanding of the conditions sufficient for equilibrium and, ultimately, to prove that they are necessary as well. I will discuss cases of cross-fertilization between the different approaches in 1871 (sections 3.1, 3.2, 3.3) and their role in constructing the Boltzmann equation of 1872 (section 3.5).

The reconstruction of the often neglected preparatory studies to the 1872 theory shows that the Boltzmann equation and the H-theorem were the fruits of a continuous interplay between mechanical and probabilistic arguments and were by no means understood as mere mechanical laws.

The analysis of the road to the 1872 theory occupies the most substantial part of the paper (sections 2 - 3), but it is only my first argument against the mechanistic slumber narrative. In the second part of the paper I add further arguments that deal with other parts of the story. In section 4.1 I show that if we abandon the mechanistic slumber picture, we get room to understand a still unexplained episode, namely the genesis of the H-function. In section 4.2 I argue that there is historical evidence that Boltzmann must have been aware of the statistical meaning of the second law well before 1876 and presumably even before 1872.

Finally, in section 4.3 I discuss the role of Loschmidt's reversibility argument. I begin this section with noting that a weak version of the mechanistic slumber narrative is possible, which goes as follows. Even if we concede that Boltzmann's views were less strictly mechanistic than previously thought, the reversibility argument entailed problems which could not be possibly avoided by reading the H-theorem as a mere logical relation between premisses and consequences. Thus, the conceptual change undergone by Boltzmann's interpretation of the H-theorem was not as drastic to involve a complete change of outlook, but was significant anyhow. To remain in the metaphor, admittedly Boltzmann's slumber was not as deep as usually claimed, but he was indulging is a sort of light slumber. Against this version I argue that the connection between the H-theorem and the reversibility argument is largely a product of later interpretations. In reality a careful reading of Loschmidt's paper and of Boltzmann's response to it reveals that it was not the H-theorem to be at stake.

2. Many ways to the same target

In 1868 Boltzmann published a paper devoted to a thorough study of the equilibrium in gases.[4] This paper has been often regarded by the historians as a sort of exercise in mechanics aiming merely at extending Maxwell's distribution to more realistic cases.[5] By contrast, I will argue that in this paper Boltzmann does more than furthering Maxwell's line of thought: he works his personal approach through three different ways of attacking the issue of equilibrium and comes to the conviction that a satisfactory solution of the issue calls for a pluralistic strategy in which all methods play a role.

2.1. Playing with collisions

The first five sections of the paper, amounting to 31 pages out of 47, are occupied by the study of collisions. Following a suggestion of ter Haar, I will call it the *kinetic* approach to equilibrium.[6] The ingredients by which Boltzmann fleshes out his kinetic analysis are all probabilistic in nature. He puts forward the basic assumptions that all positions and directions of motion are equally probable (homogenity and isotropy), defines the distribution function of velocity $f(v)dv$ as the portion of time a certain particle spends with velocity v and, given the average number N of particles in the unit volume (or surface), calls $Nf(v)dv$ the number of particles in such volume or surface with velocity v over time.[7] In the background, asymptotic assumptions are at work. In particular, in this first part Boltzmann assumes that the number of particles as well as the volume are infinite and the time over which we calculate the average is very long.[8]

The kinetic argument is simple. Let us consider an arbitrary collision in which molecules enter with velocities v_1, v_2 and come out with v_1', v_2'. The inverse collision has the latter as initial velocities and the former as final ones. Boltzmann calculates the numbers of direct and inverse collisions occurring in a unit volume, which turn out to be proportional to $f(v_1) \cdot f(v_2)\phi dv_1 dv_2$ and $f(v_1') \cdot f(v_2')\phi' dv_1' dv_2'$ respectively, where ϕ, ϕ' are functions expressing the geometrical details of the collision (differential cross section).[9] To arrive at this result Boltzmann must introduce the hypothesis of *Stosszahlansatz* (assumption on the number of collisions, SZA for short) according to which the number of collisions involving molecules of velocities v_1, v_2 depends only on the product of the probabilities of

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[4]Boltzmann (1868).

[5]Klein (1973), Brush (1983).

[6](ter Haar, 1954, 359).

[7]In reality, Boltzmann works with cells in the velocity space defined by the extremes v and $v + dv$. I will speak of exact velocity for brevity's sake.

[8]The consequence of these assumptions is that one can interpret $f(v)dv$ and $Nf(v)dv$ as *actual* fraction of time and density of particles respectively or as *expected* values thereof indifferently. This is a clear example of how the asymptotic assumptions can turn the probabilistic phraseology in the deterministic one. I will come back to the interpretation of the distribution function later on (section 4.3).

[9]Boltzmann begins his kinetic analysis with a geometrical inquire of the collision process. This method has the advantage of making visible the effect of the assumptions of uniformity and isotropy on the calculation of the number of collision (cf. Dias (1994)), but its notation is often cumbersome.

each velocity. This hypothesis had been already successfully deployed both by Clausius and by Maxwell and was a basic assumption of kinetic theory.

If the number of direct collisions is equal to that of inverse collisions, the distribution of velocity will remain stable over time, therefore a sufficient condition of equilibrium reads:

$$v_2 f(v_1) \cdot v_1 f(v_2) = v_2' f(v_1') \cdot v_1' f(v_2') \tag{1}$$

The collisions are also subject to the conservation of energy $v_1^2 + v_2^2 = v_1'^2 + v_2'^2$. These two requirements can be fulfilled at the same time if the distribution function has an exponential form $f(v) \propto e^{-hv^2}$, where h is a constant.

Boltzmann repeats this argument for more and more complicate cases, such as spheres subject to external forces in a three-dimensional space, and shows that the essential of the kinetic approach to equilibrium consists of the SZA, the conservation of energy, and the equivalence of the geometrical details between collisions ($\phi = \phi'$). These basic requirements, together with the equilibrium condition, are therefore *sufficient* to get at Maxwell's distribution.

2.2. Two novel ways

In the last part of the paper the direction of the analysis changes abruptly and Boltzmann develops two outright original ways of looking at the equilibrium problem. Many commentators have found difficult to fit these pages in the general story of Boltzmann's ideas,[10] because they sound absolutely alien to everything else Boltzmann published on the subject about the same time. By contrast, we will see in the next section that the path to the Boltzmann equation goes through the interplay between the kinetic approach and the new methods presented here. For this reason I will discuss the second part of Boltzmann (1868) in depth.

The aim of the second part had been announced by Boltzmann in the introduction of the paper: to investigate the relation between the equilibrium condition, usually cast in terms of kinetic relations, from an analytical and probabilistic point of view (Boltzmann, 1909, 49). First of all Boltzmann releases the condition that number of molecules and energy are infinite: now they are both very large, but finite. This step has a momentous importance, because the mathematical treatment changes radically (Boltzmann, 1909, I, 80-81):

> [T]he probability that the velocity of one point lies within given limits and, at the same time, the velocity of another lies within other limits will be by no means the product of the two individual probabilities; rather, the second one will depend on the quantity of velocity of the first point.

Here Boltzmann puts his finger on a crucial point: if there is a finite amount of energy to be distributed over a finite number of molecules, then the accessibility of a state for each

[10]The second part of Boltzmann (1868) is hardly mentioned in classical studies like Klein (1973) or Brush (1976), whereas has received more attention in Uffink (2007).

molecule is severely constrained by the states of the remaining molecules. This entails that one has to take into account *the state of the system as a whole*. Accordingly, instead of the probability for a molecule to have a certain velocity, one has to talk about 'the probability of [a certain] distribution of velocity' $f(v_1, \dots, v_n)dv_1 \dots dv_n$.[11]

The idea of ascribing a probability to the microstate of the system as a whole triggers the shift to a new way of attacking the problem of equilibrium. Boltzmann switches from the distribution of velocity to the distribution of kinetic energy and introduces a new equilibrium condition, to wit that any change in the energy allocation must be compensated by the inverse change. It entails that the distribution is a function of the total energy only.[12] Since now the probability for a molecule to have a certain energy is constrained by the distribution of energy over the remaining molecules, it is possible to calculate the distribution by simply counting the corresponding ways of allocating energy over the molecules. This motivates Boltzmann's resort to a purely combinatorial argument.

The combinatorial argument of 1868 has received scarce consideration from the historians,[13] though it is a shining example of Boltzmann's phenomenal understanding of the subtleties of probability and arguably one of the most insightful work in mathematical physics ever written by a scholar under 25. The argument is divided into two parts. As a first introductory step, Boltzmann illustrates his line of reasoning in a simple discrete case. He supposes that the total energy be decomposed into a large number p of 'elements' of the same size ϵ, so that $E = p\epsilon$. The probability P_i that an arbitrary molecule has energy $i\epsilon$ is the ratio between the total number of ways in which the remaining energy $(p-i)\epsilon = q\epsilon$ can be distributed over the remaining molecules and the total number of ways of distributing E over the molecules. Briefly said: the probability for a molecule to have a certain energy is attained by marginalizing the states of all other molecules each of which is regarded as equiprobable.

In the general case, Boltzmann arrives at the combinatorial expression:[14]

$$P_i = \frac{\binom{q+n-3}{q-1}}{\binom{p+n-2}{p-1}} \tag{2}$$

where n is the number of molecules. Boltzmann goes on to the continuous case and lets

[11] Physically, this probability is the fraction of time the system spends in the microstate such that the first molecule lies in the velocity cell $(v_1, v_1 + dv_1)$, the second one in the cell $(v_2, v_2 + dv_2)$ and so on. Note that, $f(v_1, \dots, v_n)dv_1 \dots dv_n$ might be given a 'spatial' meaning only in terms of ensembles: $f(v_1, \dots, v_n)dv_1 \dots dv_n$ would become the number of systems in the given microstate. Therefore, talking of probability as sojourn time in a state is the most straightforward way to introduce probability for a microstate of the whole system.

[12] Curiously, this is precisely the only case in which an ideal gas is ergodic in modern terms (Penrose, 1979, 1947). Boltzmann takes for granted a conclusion which is actually very problematic.

[13] It has been object of some statistical analyses in Bach (1990), Costantini et al. (1996), and Costantini and Garibaldi (1997), but, to the best of my knowledge, the only historical accounts in which it has found place are Uffink (2007) and Badino (2009).

[14] Badino (2009).

n and p asymptotically grow to infinity. This yields the Maxwell distribution for a set of molecules moving on a surface (two dimensions).

The second step is the generalization of the previous result to particles flying around in a volume (three dimensions). Boltzmann calculates the marginalizing integral exploiting the fact that at equilibrium the distribution function for the energy depends only on the total energy. The result, apart from some misprints, is the Maxwell distribution for the energy in a volume.[15]

This brilliant combinatorial argument shows how close the equilibrium condition is linked to equiprobability (of states, but also of positions and directions), to the mutual independence of the variables, to statistical arguments, and to asymptotic assumptions.

In the last section of the paper, Boltzmann merges the combinatorial argument with dynamical considerations to get what he calls the *Allgemeine Lösung*, 'the general solution to the problem of equilibrium.' He starts from a very general and abstract system, actually a set of n material points whose behavior is described by the equations of motion:

$$\frac{dq_i}{dt} = \chi_i(p_1, \ldots, p_n), \qquad \frac{dp_i}{dt} = \lambda_i(q_1, \ldots, q_n) \tag{3}$$

where q_i are coordinates and p_i are momenta $(i = 1, \ldots, n)$. He investigates how the distribution function changes over time. After a fixed amount of time δt the system passes from the phase region $d\mathbf{q}d\mathbf{p}$ to the phase region $d\mathbf{q}'d\mathbf{p}'$ thereby:[16]

$$d\mathbf{q}d\mathbf{p} = \frac{\partial(q_1', \ldots, p_n')}{\partial(q_1, \ldots, p_n)} \cdot d\mathbf{q}'d\mathbf{p}' \tag{4}$$

The Jacobian depends on the partial derivatives $\partial q_i'/\partial q_i$ and $\partial p_i'/\partial p_i$, but as q_i', p_i' come from the original coordinates by application of the equations of motion, one can write:

$$\frac{\partial(q_1', \ldots, p_n')}{\partial(q_1, \ldots, p_n)} = 1 + \sum_i \frac{\partial \delta q_i}{\partial q_i} + \sum_i \frac{\partial \delta p_i}{\partial p_i} \tag{5}$$

where $\delta q_i = \chi_i \delta t$ and $\delta p_i = \lambda_i \delta t$. Since χ_i are functions of p_i only and λ_i are functions of q_i only, the derivatives $\frac{\partial \delta q_i}{\partial q_i}$ and $\frac{\partial \delta p_i}{\partial p_i}$ are identically zero, therefore:

$$\frac{\partial(q_1', \ldots, p_n')}{\partial(q_1, \ldots, p_n)} = 1 \tag{6}$$

This is a special case of the Liouville theorem $d\mathbf{q}d\mathbf{p} = d\mathbf{q}'d\mathbf{p}'$.[17] Now let $f(q_1 \ldots p_n)d\mathbf{q}d\mathbf{p}$ be the time spent by the system in the microstate represented by the phase region $d\mathbf{q}d\mathbf{p}$, and

[15] Uffink (2007).

[16] I adopt the notation $d\mathbf{q} = dq_1 \cdots dq_n$ and analogously for the momenta p_i to indicate synthetically the phase region.

[17] In Liouville (1838) the main stress is on the application of the theorem to a system of differential equations. Only around 1855 Liouville became fully aware of the possible application of his result to analytical mechanics (cf. Lützen (1990)). Boltzmann does not mention Liouville in his early papers, he however refers to the Liouville theorem in the *Gastheorie* Boltzmann (1898).

$f'(q'_1 \dots p'_n) d\mathbf{q}' d\mathbf{p}'$ the time spent in the region $d\mathbf{q}' d\mathbf{p}'$. By applying the Liouville theorem it follows that $f(q_1 \dots p_n) = f'(q'_1 \dots p'_n)$, namely one can calculate the distribution at time $t + \delta t$ once it is known at time t. One immediate consequence is that, at equilibrium, the distribution depends on the constants of motion only.

But the most important observation is that, if the system passes through all possible states, then the distribution function remains the same for a very long time and this implies that it is an equilibrium distribution. This assumption corresponds exactly to what we usually call the ergodic hypothesis.[18] If the ergodic hypothesis holds true, it is no longer necessary to integrate the equations of motion to know the distribution function: it is sufficient to divide the allowed phase space into equally sized regions and to carry out a combinatorial calculation over it. In this way Boltzmann traces his combinatorial argument back to a hypothesis on the dynamic behavior of the system. By translating the Liouville theorem plus the ergodic hypothesis into the equiprobability condition and the integrals over the phase-space region into the calculation of the number of permutations, Boltzmann can establish a firm formal link between a general dynamic argument and a purely combinatorial procedure.

He adds, however, that some *pathological arrangements* of the microstate are possible such that the phase variables are no longer independent and not all the allowed phase regions will be passed through. These arrangements originate exceptions to the previous arguments, but, on the other hand, are too peculiar to be seriously considered.[19]

Notice that the *Allgemeine Lösung* represents a general solution of the equilibrium problem indeed. The requirement that the distribution function depends only on the integrals of motion is *a necessary and sufficient* condition for equilibrium. The specific form of the function can be immediately calculated by a combinatorics on the phase space. Hence, in 1868 Boltzmann had at hand a combinatorial proof of the necessity of Maxwell's distribution albeit not a kinetic one. In addition, a cluster of interconnected formal procedures to derive the equilibrium distribution had become suddenly available. First, a *kinetic approach* that drew upon the well-established analysis of collision; second, a highly original *combinatorial approach* that used sophisticated probabilistic arguments; third, an *ergodic approach* based on a dynamic hypothesis which was somehow related to disorder, but whose nature was still mysterious. To unfold the riddle of equilibrium a deeper analysis of the relations between these three paths was mandatory.

3. Constructing the Boltzmann equation

In 1870 and 1871, Boltzmann spent research stays in Heidelberg and Berlin, working with G. Kirchhoff and H. Helmholtz chiefly on problems of electrodynamics.[20] He was however still struggling with the problem of understanding the results achieved in 1868 and

[18] Maxwell (1879), Ehrenfest and Ehrenfest (1911), Von Plato (1991).

[19] Boltzmann mentions the example of gas molecules lined on a straight line. If the line is perfectly straight they will continue to oscillate along it without reaching a homogeneous and isotropic distribution.

[20] Hörz and Laass (1989) (Höflechner, 1994, 20-24).

eager to pursue the development of the three interlaced approaches to equilibrium. The year 1871 was particularly productive for Boltzmann. I will especially discuss a trilogy of papers in which he explores the possibilities offered by the interplay of the kinetic, the ergodic, and the combinatorial approach. In these papers Boltzmann achieves three prime results: a more general physical model, a more general formalism, and a more general collisions mechanism. These generalizations are the building blocks of Boltzmann's theory of irreversibility.

3.1. The polyatomic molecule

The three approaches of 1868 applied to different kinds of systems. The kinetic approach dealt with particles in collisions, the ergodic with particles in free motion, and the combinatorial with possible allocations of particles into states. Therefore the first step towards a combination of these approach had to be the search for a physical model appropriate both for the kinetic and for the ergodic approach. In the first paper of the 1871 trilogy[21] Boltzmann found such a model in the polyatomic molecule. A polyatomic molecule can be interpreted both as a set of non-interacting material points in free motion (the inner interaction of the atoms constituting the molecule is expressed as a constraint) and as a system in interaction with similar systems (when considering collisions between molecules).

In the first two sections of the paper, Boltzmann shows that the Liouville theorem can be applied also to the case of systems of points in interaction to wit colliding polyatomic molecules. The fundamental trick boils down to understanding two interacting molecules as a new complex system in free motion ruled by suitable equations that fulfill the Liouville theorem.

Boltzmann assumes that the first molecule has r atoms, while the second has r^* atoms. Next he defines $2s = 3r + 3r^*$ coordinates and momenta q_i, p_i $(i = 1, \dots, s)$ which represent the state of the two molecules jointly. To fix analytically the collision conditions, Boltzmann introduces a function $\gamma(q_i)$ such that a collision is said to start or finish when $\gamma = b$. In this way the two molecules can be considered as an individual system evolving in accord with the equations of motion:

$$\frac{dq_i}{dt} = \rho_i(p_1, \dots, p_n), \qquad \frac{dp_i}{dt} = \sigma_i(q_1, \dots, q_n),$$

$(i = 1, \dots, s)$. By applying the SZA, Boltzmann states that:

$$dm = f_1 \cdot f_2 d\omega_1 d\omega_2 \gamma dt \tag{7}$$

is the number of collisions occurring in unit volume and time dt between molecules initially in the phase regions $d\omega_1, d\omega_2$ respectively.[22] On the account of an application of the

[21] Boltzmann (1871c).

[22] Of course f_1, f_2 are the distribution functions for the two kinds of molecules whereas $dq_1 \cdots dq_{s-r^*} dp_1 \cdots dp_{s-r^*} = d\omega_1$ is the phase region in which the first molecule is at the beginning

equations of motion, the molecules in $d\omega_1, d\omega_2$ at the beginning of the collision will be found in the regions $d\Omega_1, d\Omega_2$ at the end. By simply reversing the reasoning, Boltzmann states that the analogous number of collisions occurring with initial states $d\Omega_1, d\Omega_2$ is $dM = F_1 \cdot F_2 d\Omega_1 d\Omega_2 \Gamma dt$. At this point Boltzmann proves that, as in the case of free motion, $d\omega_1 d\omega_2 = d\Omega_1 d\Omega_2$, therefore the equilibrium condition $dm = dM$ yields:

$$f_1 \cdot f_2 = F_1 \cdot F_2$$

which is again the kinetic expression of the equilibrium condition. Thus, the polyatomic molecule embodies both the basic feature of the free motion (the Liouville theorem $d\omega_1 d\omega_2 = d\Omega_1 d\Omega_2$) and the fundamental equilibrium condition of colliding systems. Precisely for its noteworthy properties the polyatomic molecule was to remain the prime physical model of Boltzmann's theory.

3.2. The ergodic approach

The second paper of the trilogy is very abstract and dedicated to understand better the features of ergodicity.[23] One of the results of the *Allgemeine Lösung* was that, if the system behaves ergodically, then the distribution function depends on the integrals of motion only. On the other hand, the particles moves according to equations of their generalized coordinates. Thus, in the first part of the paper Boltzmann looks for a general formalism able to relate the two descriptions of the motion.

He considers many similar systems made of n non-interacting particles in different possible states, that is a sort of gas of polyatomic molecules. The time behavior of each system is governed by ordinary equations of motion:

$$\frac{ds_i}{dt} = S_i(s_1, \ldots, s_n) \tag{8}$$

$(i = 1, \ldots, n)$ where s_i are generalized coordinates. The number of systems in a given state $d\mathbf{s}$ at an instant t is $dN = f(t, \mathbf{s})d\mathbf{s}$. Because of the equations of motion, after a certain time $t' = t + \delta t$, these systems will be in a new state $d\mathbf{s}'$. We already know that:

$$d\mathbf{s}' = d\mathbf{s} \cdot \frac{\partial(s'_1, \ldots, s'_n)}{\partial(s_1, \ldots, s_n)} \tag{9}$$

Boltzmann knows that, if the Liouville's theorem is valid, then the distribution function will be constant over the entire trajectory and, consequently, it will be function of the integrals of motion only. Thus, the number dN can be written:

$$dN = \frac{f(\phi_1, \ldots, \phi_n)}{\frac{\partial(\phi_1, \ldots, \phi_n)}{\partial(s_1 \ldots s_n)}} d\phi_1 \ldots d\phi_n \tag{10}$$

of the collision and, analogously, $dq_{s-r^*+1} \ldots dq_s dp_{s-r^*+1} \cdots dp_s = d\omega_2$ the phase region of the second molecule.

[23]Boltzmann (1871b).

where $\phi_1, \ldots, \phi_n$ are the integrals of motion. In the expression above integrals of motion (the mechanical constraints of the system) and coordinates appears together. Now Boltzmann has at his disposal a more general formalism to deal with the coordinates and constraints at the same time. He displays the potential of this formalism with various instances.

For example, one can replace one integral with the corresponding variable, let's say ϕ_1 with s_1. This situation is equivalent to Jacobi's principle of last multiplier in which $n-1$ integrals are given out of a set of n differential equations and the last one can be used to construct the integrating factor of the remaining equation.[24] Boltzmann shows that he can construct the integrating factor in exactly the same way, so that there is a close relation between the Liouville theorem and this principle.[25]

In the second part of the paper Boltzmann comes back to the ergodic motion he had already mentioned in 1868. He notices that, in mechanics, we usually deal with trajectories whereby if one knows a certain number of coordinates, the remaining ones may be established *via* equations of motion. But one can conceive cases in which the information deriving from some coordinates is insufficient to fix the others. To substantiate this thought Boltzmann imagines a point moving around a centre of force attracting it with a force $(a/r) + (b/r^2)$. The resulting motion is a series of ellipses. If the angle formed by the apsidal lines of two consecutive ellipses is an irrational multiple of π, a precession of the elliptical orbit takes place and the resulting trajectory will tend to fill all the circular region between the circumferences described by the major apsis and the one described by the minor apsis. A second example, even simpler, concerns an oscillatory system with equation $ax^2 + by^2$. Also in this case, if a/b is irrational, the system tends to cover densely all the allowed space.[26]

These simple examples display an important feature of the ergodic (in this case 'quasi-ergodic') motion, namely that the coordinates 'are mutually independent (except that they confine each other within given limits)' (Boltzmann, 1909, I, 270): knowing one coordinate is not sufficient to establish the others, but we can only define a new hypersurface where it can be found. In the ergodic motion the integrals fix some coordinates, but the remaining are free to assume whatever value.

This brings Boltzmann to a further application of his formalism. In fact, it is now simple to distinguish between dependent coordinates (fixed by the constraints) and independent coordinates (free to change). Let us assume that $s_1, \ldots, s_k$ coordinates are independent and the remaining $n-k$ are fixed by the integrals $\phi_{k+1}, \ldots, \phi_n$. By applying the same

[24]Jacobi (1844), Nucci and Leach (2008).

[25]Historically, this relation is remarkable. Boltzmann envisions — and actually uses, for instance in Boltzmann (1871d) — the connection between Jacobi's principle and the concept of invariant integral (cf. Berrone and Giacomini (2003)) that would be formalized by Poincaré many years later in a work that, ironically, was to lead to the recurrence theorem, the basis of Zermelo's objection to Boltzmann's approach in mid-1890s. Both Liouville and Jacobi had seen the same connection (cf. Lützen (1990)), but it seems that Boltzmann was the first one to figure out physical applications of the theorem.

[26]Brush (1976), Uffink (2007).

argument as before, Boltzmann shows that one can express the average time spent by the system in a certain state of the independent coordinates in terms of the integrals of motion:

$$f(s_1, \dots, s_k) ds_1, \dots, ds_k = \frac{C ds_1, \dots, ds_k}{\frac{\partial(\phi_{k+1} \dots \phi_n)}{\partial(s_{k+1} \dots s_n)}} \tag{11}$$

where C is a constant. Since the independent coordinates $s_1, \dots, s_k$ may assume all values consistent with the general constraints of the problem, one needs only to know the integrals of motion 'without that be necessary to know something on the way in which $s_1, \dots, s_k$ actually change' (Boltzmann, 1909, I, 277). Equation (11) is a useful result because it gives us a very compact expression of the 'elementary' microscopic state gauged, so to say, by the integrals of the problem. Perceptively, Boltzmann points out the amazing flexibility of this equation: from it one can easily obtain any macroscopic distribution by simply marginalizing the independent variables. This is precisely the combinatorial procedure of 1868 embedded in a more general dynamical framework. In this way Boltzmann has again showed the close relation between ergodic and combinatorial approach.

As for the physical justification of the ergodic hypothesis though, Boltzmann has nothing more to offer than an appeal to the disorder of the motion (Boltzmann, 1909, I, 284):

> The great irregularity of the thermal motion and the multiplicity of the forces acting on the body from outwards make probable that its atoms [...] pass through all the possible positions and speeds consistent with the equation of energy.

The ergodic behavior must be related to the internal irregularity of the gas and to the large number of degrees of freedom, but a definite proof of the ergodic hypothesis is still a desideratum.

3.3. Generalizing the collisions

In the first two papers of the 1871 trilogy, Boltzmann focuses on the kinetic and the ergodic approach respectively. He develops a powerful formalism and the physical model of the polyatomic molecules which permits to intermingle both approaches at the same time. In the *Analytischer Beweis*, chronologically the last paper of the trilogy, Boltzmann figures out a new collision mechanism that can be regarded as the direct precursor of the Boltzmann equation.[27]

The *Analytischer Beweis* is the most studied of the papers of 1871, especially because the title allegedly suggests a shift of the emphasis to the problem of irreversibility. But apart from the issue of the analytical proof of the second law, the *Analytischer Beweis* is an important document to understand the process that led Boltzmann to frame the

[27]Boltzmann (1871a).

equation named after him. I start with analyzing in detail the collision mechanism presented in this paper because it seems that a few relevant points escaped the attention of the commentators.[28]

In the *Analytischer Beweis* the problem of collisions is studied from a new perspective: instead of balancing individual collisions between similar molecules of the same system, Boltzmann zooms in on a single molecule and investigates its behavior when colliding with molecules of a different gas in all possible conditions. This way of tackling the issue has the remarkable consequence of mingling the two interpretations of the distribution function: when Boltzmann follows the trajectory of a single molecule, he considers the fraction of time that the molecule spends on average in a certain state, while when he centers on the behavior of a set of molecule the distribution function measures the average spatial density (how many molecules in the unit volume).

The argument goes as follows. The state of a polyatomic molecule, called K to fix ideas, is described by the positions $q_1, \ldots, q_r$ and momenta $p_1, \ldots, p_r$ of its r atoms. The molecule K may interact with many other polyatomic molecules whose generic state is, again, given by the values of the positions $q'_1, \ldots, q'_s$ and momenta $p'_1, \ldots, p'_s$ of the s atoms. The behavior in time of the two kinds of systems is described by two kinds of densities. On the one hand, the average time the molecule K spends in the state $d\mathbf{q}d\mathbf{p}$ during a very long time T is given by $Tg(\mathbf{q}, \mathbf{p})d\mathbf{q}d\mathbf{p}$, where g is a suitable temporal density. On the other hand, the number of the other molecules that, in unit volume, occupy the state $d\mathbf{q}'d\mathbf{p}'$ is given by $dNd\mathbf{q}'d\mathbf{p}'$, where dN is a suitable spatial density.

Given these conditions, the number of collisions that occur between K and other molecules during T whereby both are in the *initial* states $d\mathbf{q}d\mathbf{p}$ and $d\mathbf{q}'d\mathbf{p}'$ is:

$$dm = Tg(\mathbf{q}, \mathbf{p})dN\phi d\mathbf{q}d\mathbf{p}d\mathbf{q}'d\mathbf{p}' \tag{12}$$

where ϕ is the differential cross section. Of course, such a collision reduces by one unit the number of molecules in the regions involved. After the collision, the molecule K will be found in the new state $d\mathbf{Q}d\mathbf{P}$, while the other molecule will be in the state $d\mathbf{Q}'d\mathbf{P}'$. Analogously, the function ϕ becomes $\Phi = D \cdot \phi$, where D is the Jacobian of the variables describing the state before and after the collision, as already seen in the paper on the polyatomic molecule. Likewise, the number of collisions that occur during the time T with *initial* states $d\mathbf{Q}d\mathbf{P}$ and $d\mathbf{Q}'d\mathbf{P}'$ easily follows from applying the same reasoning and the same assumptions:

$$dM = TG(\mathbf{Q}, \mathbf{P})dN'\Phi d\mathbf{Q}d\mathbf{P}d\mathbf{Q}'d\mathbf{P}' \tag{13}$$

Now Boltzmann uses the analytical relations between the coordinates before and after the collision to further manipulate this result. One moment's reflection suggests that the number of collisions occurring in T such that the molecules involved are eventually found in the states $d\mathbf{Q}d\mathbf{P}$ and $d\mathbf{Q}'d\mathbf{P}'$ is given by the formula:

[28] Illuminating remarks on other aspects of this paper can be found in Klein (1973), Brush (1983), Uffink (2007).

$$dm = Tg(\mathbf{q}, \mathbf{p})dN\phi \cdot Dd\mathbf{Q}d\mathbf{P}d\mathbf{Q}'d\mathbf{P}' \tag{14}$$

Each of these collisions increases by one unit the number of molecules in the regions. By integrating over all possible values that the variables $\mathbf{Q}'$ and $\mathbf{P}'$ can assume, Boltzmann gets the number $\int dm$ of all collisions that drag the molecule K into the state $d\mathbf{Q}d\mathbf{P}$.[29] If the same integration is performed on dM, one gets the number $\int dM$ of collisions that take the molecule K from the state $d\mathbf{Q}d\mathbf{P}$ into any other possible state.

Finally, Boltzmann verifies that the equilibrium condition $\int dm = \int dM$ is fulfilled if the density functions are:

$$g = Ae^{-hE}, \qquad dN = ae^{-hE^*} \tag{15}$$

where a, A are constants and E, E^* are the total energies. The first density gives the average amount of time the molecule K spends in any given state, the second density gives the average amount of molecules in unit volume in any given state.

In this argument Boltzmann makes extensive use of asymptotic assumptions, in particular he often insists that we have to consider a sufficiently large number of molecules and a sufficiently long time. These assumptions serve to 'typify' the argument and to eliminate exceptions.

The influence of the combinatorial approach is spottable in an illustration of the collision mechanism that Boltzmann provides at a certain point (Boltzmann, 1909, I, 291). He asks the reader to imagine the collisions taking place so rapidly that one can almost neglect the time separating two successive events. At the same time, only binary collisions occur. These assumptions are of course highly unrealistic, but the point Boltzmann is willing to make is a purely conceptual one. If one leaves out the free motion and considers only the transitions from one state to the other, then the equilibrium condition $\int dm = \int dM$ tells us that any transition pulling K out of the state $d\mathbf{Q}d\mathbf{P}$ must happen as often as any transition taking it into the same state.

This way of putting the matter together with the fact that Boltzmann is studying the dynamic behavior of a single system in interaction with a heat reservoir suggest that he is conceiving a sort of kinetic analogon of the combinatorial procedure: he is not interested in the mechanical details of the collision process, but only in the ensuing redistribution of the velocities. The success of the combinatorial argument both for the derivation of Maxwell's distribution and for the explanation of the role of analytical tools led Boltzmann to an even more daring intersection between combinatorial and kinetic approach. Moreover, this intersection is indeed a fundamental step to get the Boltzmann equation because it changes the analysis of collisions from an individual event to a class of events and paves the way to an equation of the detailed balancing. Once again, hence, the combinatorial argument works behind the scene, as a sort of heuristic tool.

[29]Note that Boltzmann must suppose that during the time T the molecule K collides with the other molecules according to all possible conditions, an assumption that he might presumably ascribe to disorder.

3.4. Preparing the leap to irreversibility

The three papers forming the trilogy of 1871 are an important document to understand the process leading to the formulation of the Boltzmann equation and of the H-theorem in 1872. On this account they should be read together, as part of a comprehensive effort to unfold the insights hidden in the 1868 paper. The previous historical analysis has revealed that Boltzmann took a pluralistic strategy in tackling the problem of equilibrium and has tried to highlight the conceptual connections between his three approaches. The immediate results of the pluralistic strategy were a more general physical model (the polyatomic molecule), a powerful formalism able to deal with ergodic motion, and finally a more refined mechanism of collisions.

On a more general ground, Boltzmann became aware that any approach has its pros and cons, but all lead to the equilibrium distribution and each of them can be used to illuminate how the others work. Thus Boltzmann investigated any specific ingredient both individually and in its connection with the others. Moreover, this challenging exploration made frequent appeal to disorder and asymptotic assumptions. In the next section, which concludes the first part of my argument, I show how these elements combine in the 1872 paper and what were Boltzmann's actual aspirations.

3.5. Putting the mosaic together: The Boltzmann Equation

We do not know much about the historical background of the famous 1872 paper in which Boltzmann puts forward his equation and the H-theorem.[30] It is established that the essence of the paper was written during his stay in Berlin. In a famous letter to his mother Katharina on 27 January 1872, Boltzmann writes about having presented an outline of the paper before the Berliner Physikalische Gesellschaft. However, the talk attracted no attention, except for some remarks of Helmholtz:[31]

> Yesterday I spoke at the Berlin Physical Society. You can imagine how hard I tried to do my best not to put our homeland in a bad light. Thus, in the previous days, my head was full of integrals. [...] Incidentally there was no need for such an effort, because most of the listeners would have not understood my talk anyway. However, Helmholtz was also present and an interesting discussion developed between the two of us.

From another letter to Josef Stefan on 2 February 1872 we also know that Boltzmann was bothered about loosing the priority, after all an understandable worry for an ambitious young scholar. For this reason he had worked out the paper in a hurry and intended to publish the talk in the *Annalen* and a lengthier, elaborated version in the *Wiener Berichte* (Höflechner, 1994, II, 10-11). On the insistence of Stefan, Boltzmann eventually resolved to publish the paper only in the *Wiener Berichte* and sent off to the *Annalen* an account of his studies on electrodynamics.

[30] Boltzmann (1872).
[31] (Höflechner, 1994, II, 9), Cercignani (1998).

These scant pieces of information establish two points relevant for our discussion. First, the 1872 paper was elaborated in the same breath with the cluster of reflections and analyses that found place in the 1871 series. Thus, it is part and parcel with the pluralistic strategy and it should be read together with its 1871 predecessors. Secondly, for contingent reasons — worries about the career, concomitant work on other subjects — the paper was written under pressure. This circumstance should encourage a contextualization of the work and discourage too literal a reading.

Let us now see how the different threads elaborated in 1871 are interwoven in the 1872 paper. In the introduction Boltzmann lays down the essential message of the work. The aim is to find the necessary and sufficient conditions for attaining Maxwell's distribution. Accordingly, the argument has a strong emphasis on the inferential structure: Boltzmann investigates the logical relation between some assumptions and their consequences. Moreover the argument is essentially probabilistic in nature and this fact deserves a specific discussion:[32]

> [T]he problems of the mechanical theory of heat are also problems of probability theory. It would, however, be erroneous to believe that the mechanical theory of heat is therefore afflicted with some uncertainty because the principles of probability theory are used. One must not confuse an incompletely known law, whose validity is therefore in doubt, with a completely known law of the calculus of probabilities; the latter, like the result of any other calculus, is a necessary consequence of definite premises, and it is confirmed, insofar as these are correct, by experiment, provided sufficiently many observations have been made, which is always the case in the mechanical theory of heat because of the enormous number of molecules involved.

This passage is very explicit in showing the tight relation between theory of heat and probability and the inferential structure of the argument. Boltzmann sees a probabilistic theory as a perfectly exact theory in the sense that *the consequences follow logically from the premises*, therefore the conclusions that one can draw from the initial assumptions are not undermined by the fact that one is using probabilistic arguments. Another point mentioned in the quotation concerns the physical plausibility of these assumptions. Here and in other passages of the paper, Boltzmann relies on the asymptotic character of the problem: gases are constituted of a huge number of molecules, we can take volumes and observation time as large as we please. These conditions make intuitively clear that averages will be stable, that the behavior of a single molecule in time is the same as the instantaneous behavior of a set of molecules, that molecules get progressively mixed and so on. Taken for granted these conditions, the argument merely goes on by drawing the logical conclusions. In this regard, there are two points I would like to make.

First, it was well known that, in statistical reasoning, pathological microscopic arrangements exist that can possibly lead to odd behaviors. Boltzmann himself had discussed

[32](Boltzmann, 1909, I, 316-317).

examples of these pathological arrangements at the end of Boltzmann (1868) (section 2.2). As said, the asymptotic conditions were supposed to dispose of these arrangements or, at least, to confine them to the realm of purely theoretical possibilities. Secondly, the previous quotation clarifies that when Boltzmann ascribes 'necessity' to his conclusions he means *the internal necessity of his inferential argument*, namely the logical necessity and the physical necessity insofar the asymptotic conditions are fulfilled.

As an illustration of how Boltzmann constructs his 1872 argument we can take the case of monoatomic gas. He insists that there are only two general assumptions. First, all directions of motion are equally probable (isotropy), second, the molecules are uniformly distributed over all possible positions (homogeneity). In both cases, Boltzmann points out that, even though at the beginning such conditions may not hold true, the effect of the collisions is precisely to equalize directions and positions. This means that the equiprobability should be understood as an equal tendency of the molecules to assume directions and positions in consequence of the collisions. This point is important because in the second part of the paper Boltzmann plans to deal with transport phenomena and the equal tendency based on collisions allows him to introduce a non-homogeneous distribution function without major changes in the mechanism of equilibration. Hence, the inferential structure of Boltzmann's argument is the following: he shows that the equilibration of velocity follows from the assumed equilibration of positions and directions of motion.

The derivation of Boltzmann's equation is well known. The state of the system is described by the spatial density $f(v_1,t)d^3v_1$ of molecules that have velocity v_1 at the time t. Boltzmann evaluates the temporal variation of $f(v_1,t)d^3v_1$ by applying a version of the collision mechanism worked out in the *Analytischer Beweis*. The variation is given by the balancing between the molecules gaining velocity v_1 and those loosing it as an effect of collisions, therefore Boltzmann calculates the total number of collisions during the time τ that have v_1 as starting velocity and compares it with the number of collisions that have v_1 as final velocity. These numbers are, respectively:

$$\int dn_1 = \tau dv_1 \int_0^{\infty} \int_0^{v_1+v_2} d^3v_2 d^3v_1' \psi(v_1, v_2, v_1') f(v_1,t) f(v_2,t) \tag{16}$$

$$\int dn_2 = \tau dv_1 \int_0^{\infty} \int_0^{v_1+v_2} d^3v_2 d^3v_1' \psi(v_1', v_2', v_2) f(v_1',t) f(v_2',t) \tag{17}$$

where v_2 is the velocity of the second molecule, v_1', v_2' are the velocities of the molecules after the collision and ψ is the differential cross-section. By series expanding $f(v_1,t)$ at the point v_1 and neglecting higher order differentials, it can be show that:

$$\frac{\partial f(v,t)}{\partial t} = \int dn_2 - \int dn_1 \tag{18}$$

therefore a time equation for $f(v,t)$ may be obtained by directly comparing the two numbers of collisions. Here Boltzmann deploys the results arrived at in Boltzmann (1871b) and Boltzmann (1871c) and notices that the function ψ must fulfill the Liouville theorem for collisions. This means that ψ remains the same for both types of collisions and the time variation of the distribution function can be written as a balancing between the distributions of the velocities involved in the collision:

$$\begin{aligned}\frac{\partial f(v,t)}{\partial t} &= \int_0^\infty \int_0^{v_1+v_2} d^3v_2 d^3v_1' \psi(v_1,v_2,v_1')[f(v_1',t)f(v_2',t) \\ &- f(v_1,t)f(v_2,t)]\end{aligned}$$

This is the famous Boltzmann equation. It is easy to prove that Maxwell's distribution fulfills the equilibrium requirement $\partial f(v,t)/\partial t = 0$, therefore the initial conditions assumed by Boltzmann are sufficient. To prove that they are also necessary, Boltzmann must show that Maxwell's distribution is the only equilibrium distribution. To accomplish that, he figures out the H-theorem. He introduces a special function of f, namely $H = \int dv f(v,t) \log f(v,t)$ and shows that its time derivative must decrease monotonically to a minimum value, corresponding to Maxwell's distribution.[33] I will say more on the H function and on the theorem in the following sections, but now I would like to discuss Boltzmann's comments on this outstanding result.

Boltzmann promptly points out that '[H] must necessarily decrease' and therefore, 'it has 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.'[34] This emphasis on necessity seems to suggest that Boltzmann understands his result as free of exceptions, but on a careful consideration, one realizes that the issue of physical exceptions has no room whatever here: Boltzmann is talking about the logical necessity of the relation between the initial assumptions and the conclusions of the theorem. In fact, he states that the theorem holds *for any arbitrary distribution of velocity, not for any arbitrary microscopic arrangement*. The problem of the pathological arrangements has been simply left out of the inferential argument: Boltzmann does not mention exceptions because they are excluded from the start. This can be clearly seen from the emphasis put on the fact that the monotonic decrease of H takes place 'in the course of a very long time.' This qualification suggests that Boltzmann is appealing to asymptotic conditions.[35]

[33]Famously in 1872 Boltzmann proposes the letter E whereas the letter H we used today was first introduced by Burbury. Moreover, in Boltzmann's paper the function reads $H = \int dv f(v,t)[\log f(v,t) - 1]$ because the term -1 simplifies a bit the calculation. The term, however, is not strictly necessary because the additional integral $\int \partial f(v,t)/\partial t$ coming out from the time derivative of H can be eliminated by appealing to the conservation of the total number of molecules. Boltzmann mentions this point in a footnote.

[34](Boltzmann, 1909, I, 345).

[35]In the paper Boltzmann does not justify the claim that H must decrease only after a very long time. On the contrary, it is well known that the collision term of the generalized Boltzmann equation changes very rapidly (cf. Cohen (1962)). Thus, it seems that the addendum has more to do with the character of monotonicity, which holds true in the long run.

Interestingly, similar provisos to the theorem are added by Boltzmann when he turns to the discrete case. He points out that the H-theorem for the discrete amounts of energy shows that the distribution tends to reach the equilibrium after a very long time and 'with the exception of very special cases', namely pathological micro-arrangements.[36]

Furthermore, Boltzmann cautions the reader against too a literal understanding of the theorem for the monoatomic gas. He highlights that, in this case, 'the procedure used [...] is of course nothing more than a mathematical artifice.' A physical meaning of this argument, Boltzmann states, can be gained by applying it to the case of polyatomic molecule. This is unsurprising because, as we have seen, the polyatomic molecule was considered by Boltzmann as the proper physical model for his multifaceted theory.

In the second and third part of the paper Boltzmann makes extensive use of the analytical machinery developed in 1871. To treat the transport phenomena, for instance, he exploits concepts introduced for the polyatomic molecule. The generalized distribution function $f(q, v, t)d^3qd^3v$ depends on the velocity as well as on the position because of the local differences in density. A generalized Boltzmann equation is obtained by combining the free evolution of the local volumes (streaming term) with the collision term and the analytic arsenal developed for the polyatomic molecule is applied to the problem of transport phenomena. The same arsenal comes explicitly to the fore in the third part where Boltzmann generalizes the H-theorem to the polyatomic molecule. However also in these cases, he shows that the argument retains its inferential structure.

In summary: admittedly in the 1872 paper Boltzmann uses a terminology that apparently does not leave room for exceptions, but in evaluating this paper we should take into account two factors. First, the main point is to establish the sufficient and necessary conditions for equilibrium, therefore Boltzmann is more interested in the logical relations between premises and consequences. The issue of the physical occurrence of the premises is pushed back to the asymptotic conditions. Secondly, it should be remembered that the kinetic approach was part of a more comprehensive pluralistic strategy and the Boltzmann equation was the result of this strategy. Although in the kinetic approach the issue of exception is not tackled directly, it is always present because it affects both the ergodic approach and the combinatorial approach which are part and parcel with Boltzmann's understanding of equilibrium.

4. Further arguments against the statistical turn

4.1. Turning the chronology upside down

The emergence of the H-theorem is a long-standing mystery. As it stands in 1872, the theorem consists merely in stating the suitable H-function and in plunging it into the Boltzmann equation to show that it has the desired properties. In other words, given the correct function the theorem becomes an analytical statement whose validity is constrained by the validity conditions of the Boltzmann equation. It is clear that Boltzmann had no

[36] (Boltzmann, 1909, I, 357-358).

argument to derive that function on the ground of the dynamics of the system. Therefore, the question: how did he find out the correct H-function? The usual answer resorts to a pure flash of genius. Stephen Brush has ventured the hypothesis that the H-function was 'a brilliant inspiration' and suggested that it was 'probably the result of educated guesses on his previous work with entropy formulae, combined with some trial-and-error work.'[37] As disappointing as it may appear, this is what we have at hand so far. Most of other historians have simply restrained from advancing hypotheses and have taken the H-function as a miraculous gift of Boltzmann's ingenuity.

The 'mechanistic slumber narrative' is a serious obtacle to any plausible guess on the birth of the H-function. Indeed, it pictures Boltzmann's pre-1877 work as nothing but purely mechanical and, since there is no clear mechanical way to arrive at the function, we are only left with the option of the flash of genius. But as soon as we release this constraint and concede the possibility that Boltzmann attained the H-function through statistical arguments, new possibilities become available. I will put forward here a conjecture on the genesis of the H-function that draws upon Boltzmann's wholesale use of probabilistic arguments before 1877. Admittedly, it has no direct support, but it borrows plausibility from my general argument. The conjecture runs as follows.

We have seen that Boltzmann had the solution to the uniqueness of Maxwell's distribution as early as 1868. In the last page of the paper he remarks that the combinatorial argument 'fills a gap of all others derivations' because 'it shows not only that for [Maxwell's] distribution of velocity the equilibrium takes place, but also that the [equilibrium] is possible in no other way.'[38] He thus knew very well that the uniqueness of Maxwell's distribution followed from the fact that it is the most probable one, to wit compatible with the largest number of microscopic configurations.

If we look at the way in which Boltzmann entwined mechanical and probabilistic arguments, it becomes reasonable that he had elaborated the H-function already around 1870. Looking for a solution to the problem of uniqueness, Boltzmann might have resorted again to combinatorial arguments as a heuristic tool. In particular, he might have asked for a function of the distribution which becomes an extreme (a maximum or a minimum) for Maxwell's distribution only. This problem is very difficult in the kinetic approach, but rather accessible in the combinatorial one: Boltzmann could have solved this problem by and large with a procedure very similar to that used in 1877 i. e. by calculating the state probability and by maximizing it. He could have realized very soon that the state probability can be written:

$$W = \frac{N!}{\prod n_i!} \tag{19}$$

where N is the total number of molecules and n_i is the number of molecules in the i-th energy cell. From this formula (plus the Stirling approximation) it is immediate to conclude

[37](Brush, 1976, 600).
[38](Boltzmann, 1909, I, 96).

that $\log W$ is a maximum when the function $\sum n_i \log n_i$ is a minimum. But this function is precisely the H-function.

It is important to notice that this procedure does not require conceptual resources unknown to Boltzmann in early 1870s. Moreover, this argument is not essentially different from the one put forward in 1868, which also relied on counting the number of microscopic configurations compatible with some state.[39] If we admit, contrary to the mechanistic slumber narrative, that Boltzmann took seriously the combinatorial arguments as a heuristic tool, then the conjecture sketched above becomes plausible. Furthermore, we do not need to assume that Boltzmann had a full-fledged version of the 1877 theory already at his disposal before 1872, but only the fundamental idea. If this is the case, Boltzmann might have realized *via* combinatorial reasoning that the minimum of the function $H = \int dv f(v,t) \log f(v,t)$ corresponds to the maximum of probability and therefore to Maxwell's distribution. At this point, only an integro-differential equation for $\partial f(v,t)/\partial t$ was necessary to complete the argument and that was achieved through an interplay between kinetic, ergodic, and combinatorial approach.

This conjecture allows us to dispose of some puzzles. First, as already reminded, there is no account for the genesis of the H-theorem apart from those based on the flash of genius or trial-and-error. Secondly, in the 1877 paper Boltzmann uses equation (19) to define the probability of state, but, amazingly, there is no comment whatever on the identity between the denominator of the state probability and the H-function. It is rather baffling that Boltzmann does not even remark on the formal similarity, even more so if he had discovered it for the first time in 1877 through a combinatorial way. Instead, according to my conjecture he had not reason to comment because the H-function had originally been derived along the same line.

Beside its illuminating power, another support for this conjecture comes from the historical analysis of Boltzmann's work in 1871 and his pluralistic strategy. In the foregoing sections we have seen that time and again Boltzmann fell back to ergodic and combinatorial approaches to improve the kinetic approach. Combinatorially, the proof of uniqueness was rather straightforward, it is therefore reasonable that Boltzmann looked at a combinatorial path to solve the problem and successively tried to integrate this path in the kinetic approach. This conjecture has thus the advantage of making the genesis of the H-function consistent with Boltzmann's overall strategy.

4.2. Sympathy for the demon

A serious problem of the mechanistic slumber narrative is that there is substantial historical evidence that the limitations of the second law were known to the leading experts of kinetic theory well before 1876. Specialists in theory of gas made extensive reference to

[39] Indeed, in an interesting paper published in 1910 Wilhelm Lenz shows the amazingly close connection between the combinatorial arguments of 1868 and 1877 (Lenz (1910)). For a recent comparison see Badino (2009).

the disorder of the gaseous motion and this notion was often related to probability.[40] It is therefore unsurprising that many physicists in the field began to think, around the same years, that the second law, after all, had only a statistical meaning.

This holds true for Boltzmann's circle of scientific acquaintances as well. In 1869, Josef Loschmidt, Boltzmann's colleague at the Physics Department of the University of Vienna and his close personal friend, published a paper in which an 'inanimate' version of Maxwell's demon is presented Loschmidt (1869). The crucial point, Loschmidt notices, is that our physical description deploys average values, for instance of the energy, and this means that at a microscopic level some particles have an energy above the average, some have one under the average. It is therefore possible to induce macroscopic changes in the system by a suitable selection procedure. Loschmidt supposes a volume V separated into two sub-volumes by a partition. The selection procedure works as follows:[41]

> If the initial states of all molecules in V are known, then the molecules hitting on a particular unit surface σ in any ensuing instant are completely determined. Now we assume that at the position of σ an opening in the partition is placed, which is able to open and close at deliberate moments; it is thus possible to arrange this device so that only those molecules will enter [a sub-volume v] whose velocity is higher that the mean value c and will be even possible to increase their number so that also the gas density in v will become higher than that in V. It is therefore theoretically possible to raise a gas from a lower to a higher temperature or to increase its density without expense of work or specific compensations.

We know for certain that Boltzmann was well aware of this argument from the outset. During his stay in Berlin he published a long review paper in *Die Forschritte der Physik*, the official journal of the Berlin Physical Society, in which he discussed the most significant publications on the theory of heat for the years 1869-1870.[42] Loschmidt's paper is awarded of a long and detailed review that focuses chiefly upon some chemical consequences. At the end of the review Boltzmann summarizes the argument of the 'demonic' device and points out the main consequence:[43]

> For example, if a gas at constant temperature is divided into two parts by a partition with a small hole, it would be possible to place a device before the hole which lets the faster molecules enter in a part, the slower in the other and separates the gas into a warmer and colder part, which would contradict the second law.

[40]Similar appeals to the irregularity of motion can be found in Boltzmann's first paper on the second law Boltzmann (1866), as well as in Clausius's papers on the application of mechanics to kinetic theory Clausius (1859, 1870, 1871).

[41](Loschmidt, 1869, 401).

[42]Boltzmann (1870). Note that this article has not been included in Boltzmann's Collected Papers.

[43](Boltzmann, 1870, 470).

The possibility of a violation of the second law was thus discussed in Boltzmann's institute before 1872. Furthermore, in 1871 Maxwell published his *Theory of Heat* in whose penultimate section the argument of the demon is presented and the statistical meaning of the second law explicitly stated.[44] Since Boltzmann followed with the greatest attention Maxwell's work, it is highly implausible that he did not know this important book.

Further information on the lively exchange of ideas in the second law at the Viennese Physics Department comes from a speech in memory of Loschmidt that Boltzmann held on July 8, 1895.[45] In this text Boltzmann colorfully relates that Loschmidt introduced the violation of the second law before Maxwell and that his argument was superior to that of the English physicist. In fact, Boltzmann did not like the dependence on a foreign intelligence because:[46]

> [I]f all differences in temperature have been equalized, no intelligent entity could any longer exist. In a cellar at uniform temperature, I said, no intelligence can be present. As it were today, I see before me Stefan [the director of the Physics Department], who had remained silent during our lively quarrel, commenting laconically: 'Now I realize why your experiments with the big glass tubes in the cellar have failed so deplorably.'

This document evidences that discussions on the limitations of the second law were order of the day in Stefan's department around 1872. More interestingly, in Boltzmann's passionate recollection of the accomplishments of Loschmidt the argument is repeatedly mentioned, but he never alludes to any effect on his own outlook of the problem. There would have been no better occasion of a memorial speech in honor of his lifelong colleague and friend to admit a change in his conception of the second law and H-theorem due to the force of Loschmidt's argument. But nothing similar happened.[47] Loschmidt's argument is presented as an intriguing reflection, but not as a decisive step towards a new understanding of the nature of the second law.

All this evidence proves that Boltzmann was aware of the limitations of the second law well before 1876 and even before 1872. More specifically, he knew that some microscopical arrangements can always be conceived that entails the break-down of the law. At the same time, however, he could think that these arrangements are related to mysterious entities or to some pathological states of the system and that asymptotic conditions, or something of the kind, could rule out all pathological cases. In other words, the asymptotic conditions allowed him to define a specific set of cases in which the problem of pathological arrangements could be safely ignored. As we will see in the next section, he was not the only one to claim this view.

[44] (Maxwell, 1871, 308-309).
[45] Boltzmann (1905).
[46] (Boltzmann, 1905, 231).
[47] The same is true for a second speech Boltzmann held on November 5, 1895 (Boltzmann, 1905, 240-252).

4.3. Of drawing and counting

To be sure, 1876 was not likely the first time Boltzmann heard of the reversibility argument. Most probably he was aware of an interesting paper that William Thomson published in *Nature* on April 9, 1874.[48] In this paper Thomson discusses minutely the argument of Maxwell's demon and its meaning for the second law.[49] At a certain point he even presents an early version of the reversibility argument:[50]

> Suppose now the temperature to have become thus very approximately equalized at a certain time from the beginning, and let the motion of every particle become instantaneously reversed. Each molecule will retrace its former path, and at the end of a second interval of time, equal to the former, every molecule will be in the same position, and moving with the same velocity, as at the beginning; so that the given initial unequal distribution of temperature will again be found, with only the difference that each particle is moving in the direction reverse to that of its initial motion. This difference will not prevent an instantaneous subsequent commencement of equalization, which, with entirely different paths for the individual molecules, will go on in the average according to the same law as that which took place immediately after the system was first left to itself.

This passage hints at many intriguing points. First, Thomson alludes to the fact that, after having reached the initial state, the system will go on to a new uniform distribution of temperature albeit through a different path. This means that reversibility undermines equilibrium only locally. Boltzmann would claim the same some years later. Second, Thomson somewhat parallels the reversibility argument with the demon argument in considering both as external interventions and 'very special' cases. The behavior of the system 'left to itself' is entirely different and Thomson claims that if the number of molecules approaches infinity, the physical plausibility of the argument become negligible: 'the greater the number of molecules, the shorter will be the time during which the disequalizing will continue; and it is only when we regard the number of molecules as practically infinite that we can regard spontaneous disequalization as practically impossible.'

Thus Thomson admits that the demon argument and the reversibility argument prove the theoretical possibility of violation of the second law. To be sure, he even evaluates — qualitatively and quantitatively in a very particular case — the probability of such violation. In general, however, he relies on the asymptotic conditions to discard these conclusions from the realm of the physical possibilities. When molecules grow to infinity, such a coherent behavior becomes implausible.

[48] Thomson (1874).

[49] He hypothesizes an 'army' of demons to select suitable molecules and to change artificially the distribution of temperature in a system.

[50] (Thomson, 1874, 442).

Before moving on to present Loschmidt's use of the reversibility argument, I would like to discuss the 'light slumber' narrative I mentioned in the introduction. One might concede that Boltzmann was aware of a certain statistical meaning of the second law and that his deterministic language in 1872 only referred to the logical structure of the theory, but these concessions notwithstanding, the reversibility argument rises genuine problems for the H-theorem. In fact, it provides a powerful algorithm to construct counterexamples to the H-theorem even when the two fundamental assumptions of isotropy and homogeneity (and the asymptotic conditions as well) hold true. So, an inferential reading of the H-theorem could not save Boltzmann from facing the limitations of his theory. More importantly, the reversibility argument forces to reconsider the application of the SZA, the assumption at the root of the Boltzmann equation. Brown, Myrvold, and Uffink have egregiously summarized the challenges implicit in the reversibility argument (Brown et al., 2009, 181):

> What the Loschdmidt objection does is to demonstrate that Boltzmann's use of the H-theorem is seriously *incomplete*. First, there is no reason given as to why the SZA holds for pre-collision velocities rather than post-collisions ones. But secondly, and more to the point, so far there is no categorical reason to think that it could not be a contingent fact (unexplained for sure) that the SZA in its standard form holds at all times.

Thus, there may be a bottom line of truth in the mechanistic slumber, after all. Loschmidt's argument convinced Boltzmann that his interpretation of the H-theorem was insufficient and that the statistical illness affected the SZA as well. The light slumber shares with the deep one the claim that in 1877 Boltzmann's interpretation of the H-theorem underwent a drastic conceptual modification because of Loschmidt's criticism, although it fine-tunes the shape of this modification.

However I do not think that the light slumber narrative is tenable either. It hinges on a relation between the reversibility argument and the H-theorem that is largely an outcome of later discussions. On the contrary, *Loschmidt's original use of the reversibility argument is not directed against the H-theorem and, unsurprisingly, Boltzmann's response to it does not concern the theorem either*. To understand this point we must look carefully into Loschmidt's papers.

The main target of the series of four papers[51] published between 1876 and 1877 is a prime consequence of Maxwell's distribution: the equipartition theorem. Loschmidt finds extremely difficult to believe that, in real physical systems, the average energy of each degree of freedom is the same. In particular, he does not accept the barometric law, the statement that the average energy ascribed to each vertical level is constant when the system, for instance a column of gas, is subject to a gravitational field. Kinetic theory and the machinery of the distribution function work well for properly idealized systems. But the introduction of external forces changes everything. In his opinion, the effect of

[51]Loschmidt (1876).

external forces cannot possibly be described by the simple distribution law, but must affect the selection of microscopic states.

In the first paper Loschmidt conceives counterexamples to the barometric law based on peculiar vertical arrangements that are possible for solids but, he concedes, are extremely improbable in the case of free moving molecules. Therefore he translates the same idea into another argument. Let us imagine a vessel in which one single atom is placed at the top and the others are at rest at the bottom. The atom falls and hits the remaining so that, after a while, its potential energy is turned into kinetic energy and distributed among all atoms of the gas.

Let us now suppose to divide the total volume into horizontal layers located one above the other. The barometric law states that the mean energy of each layer — namely the total energy of the layer divided by the number of atoms in the layer — must be the same. However, Loschmidt argues, no atom can be at the top of the vessel because such a condition is compatible only with the fact that one atom is at the top and all remaining are at rest at the bottom. Interestingly, Loschmidt writes that 'it is very probable that, insofar [the number of atoms] is considerably larger than one, an atom will never come at the top.'[52] Thus, Loschmidt shares the intuitive contention that if the number of atoms is large the probability of this peculiar arrangement is very low. But he wants to explore the limits of this contention.

It is here that the argument of reversibility comes in handy.[53] Given the equilibrium described by Maxwell's distribution, Loschmidt argues that it is possible to conceive a new microscopical state which is still described by the same distribution, but gives rise to a completely different course of events:[54]

> If, after a sufficient time τ is elapsed from the establishment of the stationary state, we suddenly turn the velocities of all atoms in the opposite directions, then we will find ourselves at the beginning of a state to which the character of stationarity can apparently be ascribed. This would last for a certain time, but then the stationary state would start gradually to deteriorate and after a time τ we would arrive unavoidably again to our initial state.

The gist of the argument is that *the distribution function is compatible with two microscopical states that lead to completely different evolutions*. This means that the 'character of stationarity' embodied by the distribution is insufficient. The argument hits the heart of the equipartition theorem and the barometric law because it undermines the reliability of the distribution function as a description of thermodynamic phenomena and, as a consequence, entails that the barometric law is a pure artifact. Note, however, that this

[52] (Loschmidt, 1876, 138-139).

[53] Note that the reversibility argument, that now we regard as the essence of Loschmidt's work in 1876, only occupies half a page: it is mentioned in the first paper only.

[54] (Loschmidt, 1876, 139).

use of the reversibility argument does not concern the H-theorem.[55] Instead, Loschmidt's emphasis is on the fact that distribution function, so common in kinetic theory, misses important bits of information, therefore it comes as no surprise that it produces outcomes as strange as the barometric law.

Having clarified the real point made by Loschmidt helps us to understand Boltzmann's reply. In fact, Boltzmann's 1877 combinatorial theory[56] is a very disappointing answer to the reversibility argument as we now understand it. For us, the essence of the problem is that, given a distribution function describing the equilibrium state, half of the microstates corresponding to that function are the final states of a H-decreasing process and half of them are the starting state of a H-increasing process, therefore some modification in the SZA is required to warrant an asymmetry in the time evolution of H. However, Boltzmann's 1877 argument only shows that there are overwhelmingly more microstates corresponding to the equilibrium distribution than to any other distribution.[57] It is immediate to realize that this argument can not possibly offer a satisfactory answer to our reading of the reversibility challenge. It merely tells us one part of the story, without explaining why the underlying dynamics should be sensitive to probability differences. But if we set aside our modern perspective and bring Loschmidt's original point into play, the situation becomes less puzzling. Boltzmann was responding directly to Loschmidt's statement on the reliability of the distribution function: *analogously to Loschmidt's original argument, Boltzmann's 1877 paper does not concern the H-theorem at all.*

In Boltzmann's first reply[58] the reversibility argument is labelled as a 'sophism' based on a 'fallacy', which, however, leads to 'the correct understanding of the second law.'[59] Thus it contains a truth disguised as a paradox. The truth is that the distribution function leaves out bits of information about the system. The paradox, Boltzmann argues, consists in drawing the conclusion that the distribution function is therefore an unreliable tool. To unmask the sophistical nature of Loschmidt's conclusion it is necessary to calculate the numerical relation between distribution function and microstates as Boltzmann suggests in Boltzmann (1877a). Through this precise numerical relation it is easy to show that the distribution function is indeed an effective tool and its manipulation tells us something on the evolution of the system: it tells us that the equilibrium state is the most probable one, a conclusion Boltzmann had already arrived at in 1868.

It is hard for our modern eye to see Loschmidt's real point. We automatically consider the reversibility argument as an objection against the H-theorem. But taking into account

[55]To be sure, it barely concerns the second law. In the forth paper, for instance, Loschmidt points out that he is arguing against the odd consequences of the formalism of kinetic theory, not against the second law itself (Loschmidt, 1876, 213).

[56]Boltzmann (1877b).

[57]A detailed description of the argument can be found in Klein (1973); Kuhn (1978); Uffink (2007). Basically, it boils down to using equation (19) above to calculate the probability of a state in terms of the number of microscopic configurations ('complexions') corresponding to it and to maximizing this probability by the method of the Laplacean multipliers.

[58]Boltzmann (1877a).

[59](Boltzmann, 1909, II, 119).

the real object of the dispute the H-theorem disappears from the scene. Michel Janssen, has first suggested that the 1877 paper should not be regarded as a new formulation of the H-theorem, but rather as a rephrasing of the second law, an explanation of elements already, though confusingly, present in 1872.[60]

My reading goes towards a similar direction. Commentators have been impressed by Boltzmann's statement that the reversibility argument provides the correct understanding of the second law and by the fact that the 1877 approach is very different from the 1872 theory. These circumstances have contributed to the mechanistic slumber narrative. However, far from focussing on the H-theorem, the 1877 combinatorial theory unearths the meaning of the distribution function and its relation with the microstates.[61] From this point of view, it was essentially a reformulation of the point that Boltzmann had made in the *Allgemeine Lösung*, the section of the 1868 paper that had gone largely unnoticed.

A second argument in support of the thesis that Boltzmann did not perceived Loschmidt's 1876 paper as a threat against the H-theorem is that he kept using the 1872 theory even after 1877, while the combinatorial method did not play any important role.[62] An explanation of this attitude is that Boltzmann probably saw in the 'reversed' microstates the same character of artificiality he had denounced in the pathological micro-arrangements as early as 1868. On 14 December 1876 Boltzmann presented a paper that replied to all Loschmidt's weird special cases, which supposedly proved that probability theory is not applicable in presence of external forces. He concedes that arrangements can be figured out in which the state probability depends on the initial states and he refers to 'a similar example I have introduced at the conclusion of my paper *Studies ber das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten*' (Boltzmann (1876)), namely the case of molecules lined on a straight line. In short, Boltzmann knew very well that, using demons, exotic devices or simply our imagination we can force the system as a whole to behave weirdly. Even though these issues suggested caution in the conclusions of kinetic theory, Boltzmann could not help to deem these purpose-made cases as somewhat different from the 'typical' behavior.

This attitude was very persistent. As late as 1895 in his first reply to E. P. Culverwell, who was rising doubts on the H-theorem, Boltzmann wrote:[63]

> It can never be proved from the equations of motion alone, that the minimum function H must always decrease. It can only be deduced from the laws of probability, that *if the initial state is not specially arranged for a certain pur-*

[60] Janssen (2002).

[61] Brown et al. (2009) have suggested that the statistical turn involved a reinterpretation of the distribution function: from an expression of the *actual* number to the *expected* number of molecules. However, we have seen that in 1870s Boltzmann switches between two interpretations of the distribution function (density of many molecules or sojourn time of one molecule) and, more to the point, these interpretations were embedded into asymptotic assumptions where actual and expected numbers become equal.

[62] Except in Boltzmann (1884) where he uses it to deal with dissociation theory, a subject particularly suitable for the combinatorial formalism.

[63] Boltzmann (1895), italic added.

pose, but haphazard governs freely, the probability that H decreases is always greater than it decreases.

What Boltzmann realized only gradually after 1877 is that his intuitive dismissal of the pathological arrangements, largely based on the use of asymptotic conditions, at some point became a sidestepping of the question. The clarification of the way in which 'haphazard' elements enter the laws of dynamical systems was required and this progressively convinced Boltzmann that the basic mechanical assumptions, particularly the SZA, must have been reinterpreted. Thus I do not dispute that Boltzmann's position in the 1890s differs from his position in 1872. However, I claim, *contra* the mechanistic slumber narrative, that this evolution was much more complex and took much more time than it is usually pictured.

5. Conclusion

The historiography on Boltzmann has been often afflicted by the temptation of using the modern understanding of the subtle problems of statistical mechanics as a key to read Boltzmann's original theory. This tendency is only natural and, to a certain degree, even recommendable, but it camouflages the pitfall of a 'creative misreading' as Janssen (2002) has emphasized. A second dangerous leaning that can be found in the literature is to look at the 1872 paper as popping fully armed out of Boltzmann's head like Minerva out of Jupiter's. In this paper I have tried to avoid these drawbacks. Instead of trusting the useful but debatable guide of Ehrenfests's retrospective outlook, I have focused upon the crucial years that preceded irreversibility theory to unfold the conceptual elements whereby the Boltzmann equation and the H-theorem were constructed.

What kind of picture comes out of this analysis? From a broader perspective, we should always remember that investigations on complex systems in the second half of nineteenth century made use of disorder and probability usually in a very intuitive fashion. In most cases, asymptotic conditions were the intuitive justifications for introducing and manipulating averages and distributions. Under these ideal conditions many problems related to exceptions became immediately dismissible. Moreover, there were very good reasons to adopt this attitude. First, statistical mechanics was a relatively young discipline in need to establish its own scientific status. In this phase foundational problems are usually swept under the rug. Secondly, no adequate conceptual tools for dealing with exceptions were at disposal. Set-theoretical or measure-theoretical approaches emerged only at the turn of the century.[64]

These points must be born in mind to justly place Boltzmann's interpretation of his own results. He worked with averages and knew very well that averages experience fluctuations and their evolution calls for some microscopic disorder. So much so, that he used probabilistic arguments to handle them. Far from falling into a mechanistic slumber, from the very beginning Boltzmann lived in a state of 'statistical insomnia': he could not avoid

[64]Von Plato (1994).

statistical arguments and probability with the consequence that they are always present at different levels of his theory even when they are not explicitly mentioned.

The specific method adopted by Boltzmann constitutes another important part of the picture. From 1868 on Boltzmann developed a pluralistic strategy in which kinetic, ergodic and combinatorial procedure were treated on the same footing. On the one hand the kinetic approach was better established in the community, on the other hand the ergodic and combinatorial approaches were more general. More importantly, in the ergodic and combinatorial approaches the issue of the uniqueness of Maxwell's distribution could be immediately solved. Therefore, Boltzmann exploited ergodicity and probabilistic arguments to improve the kinetic technique. At the same time, he was aware of the presence of limitations and exceptions (pathological arrangements, fluctuations) in the ergodic outlook as well as in the combinatorial one. Thus, he was aware of analogous limitations in the kinetic approach, but he considered them as the artificial constructions of a playful demon or of a fervent imagination.

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