REREADING LUDWIG BOLTZMANN

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1 Introduction

Ludwig Boltzmann is one of the first physicists who brought probability and statistical considerations into physics. Particularly famous is his statistical explanation of the second law of thermodynamics. However, Boltzmann's ideas on the relationship between the thermodynamical properties of macroscopic bodies and their microscopic mechanical constitution, and the role of probability in this relationship are involved and differed quite remarkably in different periods of his life. In his lifelong struggle with this problem he made use of a varying arsenal of tools and assumptions. (To mention a few: the so-called *stoßzahlansatz* (SZA), the ergodic hypothesis, ensembles, the permutational argument, the hypothesis of molecular disorder.) But the role of these assumptions, and the results he obtained from them, also shifted in the course of time. Particularly notorious are the role of the ergodic hypothesis and the status of the so-called H-theorem. Moreover, he used 'probability' in four different technical meanings. It is, therefore, not easy to speak of a consistent, single "Boltzmannian approach" to statistical physics. A full survey of these various approaches would fall beyond the bounds of this paper. I shall

concentrate here on his view on the ergodic hypothesis and its connection to probability.

1.1 The Ehrenfests on the role of the ergodic hypothesis

'Statistical physics' includes at least two roughly distinguished theories: the kinetic theory of gases and statistical mechanics proper. The first theory aims to explain the properties of gases by assuming that they consist of a very large number of molecules in rapid motion. During the 1860s probability considerations were imported into this theory. The aim then became to characterize the properties of gases, in particular in thermal equilibrium, in terms of probabilities of various molecular states. This is what the Ehrenfests, in thier famous Encyclopaedia article (1912) call "the older formulation of statistico-mechanical investigations" or "kineto-statistics of the molecule". Here, molecular states, in particular their velocities, are regarded as stochastic variables, and probabilities are attached to such molecular states of motion. These probabilities themselves are conceived of as mechanical properties of the state of the total gas system: Either they represent the relative *number* of molecules with a particular state, or the relative *time* during which a molecule has that state.

In the course of time a transition was made to what the Ehrenfests called a "modern formulation of statistico-mechanical investigations" or "kineto-statistics of the gas model", or what is nowadays known as statistical mechanics. In this latter approach, probabilities are not attached to the state of a molecule but of the entire gas system. Thus, the state of the gas, instead of determining the probability distribution, now itself becomes a stochastic variable.

A merit of this latter approach is that interactions between molecules can be taken into account. Indeed, the approach is not necessarily restricted to gases, but might in principle also be applied to liquids or solids. (This is why the name 'gas theory' is abandoned.) The price to be paid however, is that the probabilities become more abstract. Since probabilities are attributed to the mechanical states of the total system, they are no longer determined by mechanical states.

Instead, in statistical mechanics, the probabilities are determined by means of an 'ensemble', i.e. a fictitious collection of replicas of the system in question.

It is not easy to pinpoint this transition in the course of history, except to say that in Maxwell's work in the 1860s definitely belong to the first category, and Gibbs' book of 1902 to the second. Boltzmann's own works fall somewhere in the middle ground. His earlier contributions clearly belong to the kinetic theory of gases (although his 1868 paper already applies probability to an entire gas system), while his work after 1877 is usually seen as elements in the theory of statistical mechanics. However, Boltzmann himself never indicated a distinction between these two theories, and it seems arbitrary to draw a demarcation at an exact location in his work.

The transition from kinetic gas theory to statistical mechanics poses two main foundational questions. On what grounds do we choose a particular ensemble, or the probability distribution characterizing the ensemble? Gibbs did not enter into a systematic discussion of this problem, but only presented special cases of equilibrium ensembles (i.e. canonical, micro-canonical etc.) for which some special form of the probability distribution is stipulated. A second problem is to relate the ensemble-based probabilities with the probabilities obtained in the earlier kinetic approach for a single gas model.

The Ehrenfest Encyclopedia paper was the first to recognize these questions, and to provide a partial answer: Assuming a certain hypothesis of Boltzmann's, which they dubbed the *ergodic hypothesis*, they pointed out that for an isolated system with a fixed total energy the micro-canonical distribution is the unique stationary probability distribution. Hence, if one demands that an ensemble of isolated systems in thermal equilibrium must be represented by a stationary distribution, the only choice for this purpose is the micro-canonical one. Similarly, they pointed out that under the ergodic hypothesis infinite time averages and ensemble averages were identical. This, then, would provide a desired link between the probabilities of the older kinetic gas theory and those of statistical mechanics, at least in equilibrium and in the infinite time limit.

Yet the Ehrenfests simultaneously expressed strong doubts about the validity of the ergodic hypothesis. These doubts were soon substantiated when in 1913 Rozenthal and Plancherel proved that the hypothesis was untenable for realistic gas models.

The Ehrenfests' attempt to construct a coherent framework out of Boltzmann's work thus gave a prominent role to the ergodic hypothesis, suggesting that it played a fundamental and lasting role in his thinking. Although this view indeed succeeds in producing a coherent view of his multifaceted work, it is certainly not historically correct. Indeed, Boltzmann himself also had grave doubts about this hypothesis, and expressly avoided it whenever he could, in particular in his two great papers of 1872 and 1877b. Since the Ehrenfests, many other authors have presented accounts of Boltzmann's work. Particularly important are (Klein 1973) and (Brush 1976). Still, there remains much confusion about what the role of the ergodic hypothesis was in his thinking. This essay aims to provide a more accurate account on this topic.

1.2 A concise chronography of Boltzmann's writing

Roughly, one may divide Boltzmann's work in four periods. The period 1866-1871 is more or less his formative period. In his first paper (1866) Boltzmann set himself the problem of deriving the second law from mechanics. The notion of probability does not appear in this paper. The following papers, from 1868 and 1871, were written after Boltzmann had read Maxwell's work of 1860 and 1867. Following Maxwell's example, they deal with the characterization of equilibrium, by means of a probability distribution, and explored new cases where the gas is subject to a static external force, or consists of poly-atomic molecules. He regularly switched between three conceptions of probability: sometimes defined as a time average, a particle average, or in (1871b) an ensemble average.

The main result of those papers is that, by adopting the SZA, one can show that the Maxwellian distribution function is stationary, and thus an appropriate candidate for the equilibrium state. In

some cases Boltzmann also argued it was the unique stationary state. However, in this period he also presented a completely different method, which did not rely on the SZA but on the ergodic hypothesis. (1868a Section 3, 1868b, 1871b) This approach led to a form of the distribution function (conceived of as the marginal of ρ) that, when the number of particles tends to infinity, reduces to the Maxwellian form. Ensembles would not play a prominent role in his approach until the 1880's.

The next period is that of 1872-1878, in which he wrote his two most famous papers: the *Weitere Studien* (1872) and *Über die Beziehung* (1877b). The 1872 paper continued the approach relying on the SZA, and obtained the Boltzmann equation and the H-theorem. Boltzmann now claimed that the H-theorem provided the desired theorem corresponding to the second law. However, this claim came under a serious objection due to Loschmidt's criticism of 1876. The objection was simply that no purely mechanical theorem could ever produce a time-asymmetrical result. Boltzmann's responded to this objection in 1877a and 1877b.

The upshot was that Boltzmann rethought the basis of his approach and in 1877b produced a conceptually very different analysis (the permutational argument) of equilibrium and evolutions towards equilibrium, and the role of probability theory. The distribution function, which formerly represented the probability distribution, was now conceived of as a stochastic variable (nowadays called a macrostate) subject to a probability distribution. That probability distribution was now determined by the size of the volume in phase space corresponding to all the microstates giving rise to the same macrostate, (essentially given by calculating all permutations of the particles in a given macrostate). Equilibrium was now conceived of as the most probable macrostate– instead of a stationary macrostate. The evolution towards equilibrium could then be expressed as an evolution from less probable to more probable states.

The third period is taken up by the papers Boltzmann wrote during the 1880's. During this period, he abandoned the permutational approach, and went back to an approach that relied on a

combination of the ergodic hypothesis and the use of ensembles. For a while Boltzmann worked on an application of this approach to Helmholtz's concept of monocyclic systems. However, after finding that these systems did not always provide the desired thermodynamical analogies, he abandoned this topic again.

In the 1890s the reversibility problem resurfaced again, this time in a debate in the columns of *Nature*. This time Boltzmann chose an entirely different line of counterargument than in his debate with Loschmidt. A few years later, he entered into a debate with Zermelo on the recurrence objection. The same period also saw the publication of the two volumes of his *Lectures on Gas Theory*. In the final years of his life he gave various formulations of the cosmological speculation. His last paper, the Encyclopedia article he wrote with Nabl, is also notable.

2 Boltzmann 1866-1871

1866: the mechanical meaning of the second law Boltzmann's first paper (1866) on statistical physics is entitled "on the mechanical meaning of the second law of heat theory". Although the results of this youthful work were rather rough, the paper is still interesting since it reveals the goals that he originally set himself and the set of ideas and methods by which he hoped to achieved them. For the present purpose, it suffices to note

He considers an arbitrary thermal body consisting of N particles and provides a mechanical definition of temperature T, which he identifies with the average kinetic energy of a particle. But unlike Maxwell, whose work was as yet unknown to him, he chose to average over *time* instead of over the number of particles in the gas. Thus, temperature is defined as

$$T = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \frac{mv^2}{2} dt =: \overline{E_{kin}}$$

(In modern notation, this means he is adopting units such that the Boltzmann constant $k = 2/3$).

Here the limits t_1 and t_2 are to be taken in such a way as "to obtain independence of any contingencies in the kinetic energy"(Abh. I, p. 14), i.e. they should cover a representative portion of the particle's motion. Note that temperature is thus a mechanical property of a single particle. In principle, this could lead to a different temperature being assigned to each particle. But Boltzmann seems to assume implicitly that the time average is the same for all particles.

The aim of the paper was to argue (under certain assumptions) that T thus defined provides an integrating divisor for the inexact heat differential $đQ$. It is not difficult to point out defects in the argument, but that is not our concern here. Note that Boltzmann nowhere uses the concept of probability. True, it talks about averages, and to some readers this might imply an implicit invocation of probability theory (e.g. von Plato 1994, p. 76). But I think that this overlooks the fact that the time-average of the kinetic energy of a molecule is an ordinary mechanical quantity that does not depend on any non-mechanical concepts for its definition.

1868: From a system of hard discs to the ergodic hypothesis Maxwell had derived his equilibrium distribution

$$f(\vec{v}) = A^3 e^{-v^2/B}, \tag{1}$$

for two special gas models (i.e. a hard sphere gas in 1860 and a model of point particles with a central r^5 repulsive force acting between them in 1867). He had noticed that the distribution, once attained, will remain stationary in time (when the gas remains isolated), and had argued (but not very convincingly) that it was the *only* such stationary distribution.

In the first section of his (1868a), Boltzmann aims to reproduce and improve these results for a system of an infinite number of hard discs in a plane. He adopts from Maxwell the idea to characterize thermal equilibrium by a probability distribution. He regards it as obvious that this distribution should be independent of the position of the discs, and that every direction of their velocities is equally probable. It is therefore sufficient to consider the distribution over the

various values of the velocity $v = \|\vec{v}\|$.

However, Boltzmann started out with a somewhat different interpretation of probability in mind than Maxwell. He introduced the probability distribution as follows:

> Let $\phi(v)dv$ be the sum of all the instants of time during which the velocity of a disc in the course of a very long time lies between v and $v+dv$, and let N be the number of discs which on average are located in a unit surface area, then
>
> $$N\phi(v)dv$$
>
> is the number of discs per unit surface whose velocities lie between v and $v + dv$. (Abh. I, p.50)"

Thus, $\phi(v)dv$ is introduced as the relative *time* during which a (given) disc has a particular velocity. But, in the same breath, this is identified with the relative *number* of discs with this velocity.

This remarkable quote shows how he connected Maxwell's interpretation of the distribution function with that of his previous paper using averages over time: simply by identifying two different meanings for the same function. This equivocation returned in different guises again and again in Boltzmann's writing.[1] Indeed, it is, I believe, the very heart of the ergodic problem, put forward so prominently by the Ehrenfests. Either way, of course, whether we average over time or particles, probabilities are defined here in strictly mechanical terms, and therefore objective properties of the gas.

[1]This is not to say that he always conflated these two interpretations of probability. Some papers employ a clear and consistent choice for one interpretation only. But then that choice differs between papers, or even in different sections of a single paper. In fact, in (Boltzmann 1871c) he even multiplied probabilities with different interpretations into one equation to obtain a joint probability. But then in (1872) he conflates them again. Even in his last paper (Boltzmann and Nabl 1904) we see that Boltzmann identifies the two meanings of probability with a simple-minded argument.

Next he goes into a detailed mechanical description of a two-disc collision process. Using a two-dimensional version of the SZA, he shows that the velocity distribution is stationary if it takes the form

$$\phi(v) = 2hve^{-hv^2}, \tag{2}$$

for some constant h. This is the two-dimensional analogue of the Maxwell distribution (1).

In the next subsections of (1868a), Boltzmann repeats the derivation, each time in slightly different settings: first, he goes over to the three-dimensional version of the problem, assuming a system of hard spheres, and supposes that one special sphere is acted upon by an external potential $V(\vec{x})$. He shows that if the velocities of all other spheres are distributed according to the Maxwellian distribution (1), the probability distribution of finding the special sphere at place $\vec{x}$ and velocity $\vec{v}$ is $f(\vec{v}, \vec{x}) \propto e^{-h(\frac{1}{2}mv^2+V(\vec{x})}$ (Abh. I, p.63). In a subsequent subsection, he replaces the spheres by material points with a short-range interaction potential and reaches a similar result. Next, he assumes that two discs are acted upon by the same external force. It is shown that mutual collisions between these two discs do not disturb the equilibrium distribution (assuming that these collisions obey the SZA). This analysis is then again transposed to three dimensions.

At the end of Section I of his paper, Boltzmann suddenly switches course. He announces (Abh. I p. 80) that all the cases treated and yet untreated follow from a much more general theorem. This theorem is the subject of the second and third Section of the paper. I will limit the discussion to the third section and rely partly on Maxwell's (1879) exposition, which is somewhat simpler than Boltzmann's own.

1868 section III: the ergodic hypothesis Consider a general mechanical system of N material points, each with mass m, subject to an arbitrary time-independent potential. In modern notation, let $(p, q) = (p_1, \ldots, p_n; q_1, \ldots, q_n)$ denote position coordinates and canonical momenta (with

$n = 3N$) of the system. Its Hamiltonian is then

$$H(p,q) = \frac{1}{2m}\sum_i p_i^2 + V(q_1,\ldots,q_n) \tag{3}$$

The state of this system may be represented as a phase point (p,q) in the mechanical phase space Γ. By the Hamiltonian equations of motion, the phase point evolves in time, and thus describes a trajectory (p_t, q_t). This trajectory is constrained to lie on a given energy hypersurface $H(p,q) = E$. Boltzmann asks for the probability (i.e. the fraction of time during a very long period) that the phase point lies in a region $dp_1 \cdots dq_n$, which we may write as:

$$\rho(p,q)dp_1 \cdots dq_n = f(p,q)\delta(H(p,q) - E)dp_1 \cdots dq_n$$

Boltzmann seems to assume implicitly that this distribution is stationary. This property would of course be guaranteed if the "very long period" were understood as an infinite time limit. He argues, by Liouville's theorem, that f is a constant for all points on the energy hypersurface that are "possible", i.e. that are actually reached by the trajectory. For all other points f vanishes. Ignoring those latter points, the function f is therefore uniform over the entire energy hypersurface, and the probability density ρ takes the form of the micro-canonical distribution

$$\rho_{\mathrm{mc}}(p,q) = \frac{1}{\omega(E)}\delta(H(p,q) - E) \tag{4}$$

where $\omega(E) := \int_{H(p,q)=E} dpdq$ is nowadays known as the structure function.

In particular, one can now evaluate the marginal probability density for the positions $q_1,\ldots,q_n$:

$$\begin{aligned}\rho_{\mathrm{mc}}(q_1,\ldots,q_n) = \int \rho_{\mathrm{mc}}(p,q)\,dp &= \frac{1}{\omega(E)}\int_{\sum p_i^2 = 2m(E-V(q))} dp_1 \cdots dp_n \\ &= \frac{(\pi)^{n/2}}{\omega(E)\Gamma(n/2)}(2m(E-V(q))^{(n-2)/2}. \end{aligned} \tag{5}$$

Similarly, the marginal probability density for finding the first particle with a momentum p_1 as well as finding the positions of all particles at $q_1, \ldots, q_n$ is

$$\begin{aligned} \rho_{\rm mc}(p_1, q_1 \ldots, q_n) &= \int \rho_{\rm mc}(q,p) dp_2 \cdots dp_n \\ &= \frac{2\pi^{(n-1)/2}}{\omega(E)\Gamma(\frac{n-1}{2})}(2m(E - V(q) - p_1^2)^{(n-2)/2} \end{aligned} \tag{6}$$

These two results can be conveniently presented in the form of the conditional probability that the momentum of the first particle has a value between p_1 and $p_1 + dp_1$, given that the positions have the values $q_1 \ldots, q_n$:

$$\rho_{\rm mc}(p_1 \,|\, q_1, \ldots, q_n) dp_1 = \frac{\sqrt{\pi}\Gamma(\frac{n}{2})}{\sqrt{2m}\Gamma(\frac{n-1}{2})} \frac{(E - V - \frac{p_1^2}{2m})^{(n-2)/2}}{(E-V)^{(n-1)/2}} dp_1 \tag{7}$$

This, in essence, is the general theorem announced.

In the limit where $n \longrightarrow \infty$, and the kinetic energy per particle $\kappa := (E - V)/n$ constant, the expression (7) approaches

$$\frac{1}{\sqrt{2\pi m\kappa}} \exp(-\frac{p_1^2}{2m\kappa}) dp_1 \tag{8}$$

which takes the same form as the Maxwell distribution (1). One ought to note however, that since V, and therefore κ depends on the coordinates, the condition $\kappa = constant$ is different for different values of $(q_1, \ldots, q_n)$. Some comments on this result are in order.

1. The difference between this approach and that of the first section is striking. Instead of concentrating on a gas model in which particles are assumed to move freely except for their occasional collisions, Boltzmann here assumes a much more general model with an arbitrary interaction potential $V(q_1, \ldots q_n)$. Moreover, the probability density ρ is defined over phase space, instead of the space of molecular velocities. This is the first occasion where probability

considerations are applied to the state of the mechanical system as whole, instead of its individual particles. If the transition between kinetic gas theory and statistical mechanics may be identified with this caesura, (as argued by the Ehrenfests and by Klein) it would seem that the transition has already been made right here. But of course, for Boltzmann this transition did not involve a major conceptual move, thanks to his conception of probability as a relative time. Thus, the probability of a particular state of the total system is still identified with the fraction of time in which that state is occupied by the system. In other words, he did not yet need ensembles or non-mechanical probabilistic assumptions.

However, one should note that the equivocation between relative times and relative number of particles, which was relatively harmless in the first section of the 1868 paper, is now no longer possible in the interpretation of ρ. Consequently, the marginal probability $\rho(p_1|q_1, \ldots q_n)dp_1$ gives us the relative time that the total system is in a state for which particle 1 has a momentum between p_1 and $p + dp_1$, for fixed values of the positions. There is no immediate route to conclude that this has anything to do with the relative number of particles with the momentum p_1, unless we further assume that $V(q_1, \ldots q_n)$ is permutation invariant.

2. Most importantly, the results (7,8) open up a perspective of great generality. It proves that the probability of the molecular velocities for an isolated system in a stationary state will always assume the Maxwellian form if the number of particles tends to infinity. Notably, this proof completely dispenses with any particular assumption about collisions, like the SZA, or other details of the mechanical model involved, apart from the assumption that it is Hamiltonian.

3. The main weakness of the result is its assumption that the trajectory actually visits all points on the energy hypersurface, nowadays called the *ergodic hypothesis*. Boltzmann returned to this issue on the final page of the paper (Abh. I, p. 96). He notes there that exceptions to his theorem might occur if the microscopic variables would not, in the course of time, take on all values which are consistent with the conservation of energy. For example, the trajectory might

be periodic. However, Boltzmann argued, such relations would be immediately annihilated by the slightest disturbance from outside, e.g. by the interaction of a single free atom that happened to be passing by. He concluded that these exceptions would thus only provide cases of unstable equilibrium.

Still, Boltzmann must have felt unsatisfied with his own argument. According to an editorial footnote in his collected works (Abh. I p.96), Boltzmann's personal copy of the paper contains a hand-written remark in the margin stating that the point was still dubious and that it had not been proven that, even allowing the disturbance from a single external atom, the system would traverse all possible values compatible with the energy equation.

2.1 Subsequent doubts on the ergodic hypothesis

In any case, the problem of the validity of the ergodic hypothesis perturbed him enough to investigate the question more closely in a special case (1868b). This paper focuses, "partly for illustration, but partly also for verification of the general theorem (Abh. I, p. 97)" on a simple mechanical system: a material point in a plane, attracted by a central potential of the form $a/r^2 + b/r^3$. Here we also find a nice pictorial formulation of the ergodic hypothesis: if the material point were a light source, and its motion exceedingly swift, the entire energy surface would appear as homogeneously illuminated (Abh. I, p. 103). Boltzmann convinces himself in this paper that the 'general theorem' in question is true in this example.

However, his doubts were still not laid to rest. His next paper on gas theory (1871a) returns to the study of a detailed mechanical gas model, this time consisting of polyatomic molecules, and avoids any reliance on the ergodic hypothesis. In fact, he subsequently noted twice that it had been a point of principle for him to avoid this hypothesis (1871b, Abh. I p.287; 1881, Abh. II p. 573). This clearly shows that Boltzmann did not trust his (1868) theorem to be sufficiently general.

And when he did return to the ergodic hypothesis in (1871b), it was with much more clarity and caution. Indeed, it is here that he actually first put forward the worrying assumption in the form of an *hypothesis*, formulated as follows:

> "The great irregularity of the thermal motion and the multitude of forces that act on a body make it probable that its atoms, due to the motion we call heat, traverse all positions and velocities which are compatible with the principle of [conservation of] energy." (Abh. I p. 284)

Note that Boltzmann formulates this hypothesis for an arbitrary body, i.e. it is not restricted to gases. He also remarks, at the end of the paper, that "the proof that this hypothesis is fulfilled for thermal bodies, or even is fullfillable, has not been provided (Abh. I p. 287)".

There is a major confusion among modern commentators about the role and status of the ergodic hypothesis in Boltzmann's thinking. Indeed, the question has often been raised how Boltzmann could ever have believed that a trajectory traverses *all* points on the energy-hypersurface, since, as the Ehrenfests conjectured in 1912, and was shown almost immediately in 1913 by Plancherel and Rozenthal, this is mathematically impossible when the energy hypersurface has a dimension larger than 1.

It is a fact that both (1868)[Abh. I, p.96] and (1871b)[Abh. I, p.284] mention external disturbances as an ingredient in the motivation for the ergodic hypothesis. This might be taken as evidence for 'interventionalism', i.e. the viewpoint that such external influences are crucial in the explanation of thermal phenomena (cf.: Blatt, Ridderbos & Redhead). Yet even though Boltzmann expressed the thought that these disturbances might help to motivate the ergodic hypothesis, he never took the idea that they are crucial very seriously. The marginal note in the 1868 paper mentioned above indicated that, even if the system is disturbed, there is still no proof of the ergodic hypothesis, and all his further investigations concerning this hypothesis assume a system that is either completely isolated from its environment or at most acted upon by a static

external force. Thus, interventionalism did not play significant role in his thinking.[2]

It has also been suggested, in view of Boltzmann's later habit of discretising continuous variables, that he somehow thought of the energy-hypersurface as a discrete manifold containing only finitely many discrete cells (Galavotti 1994). In this reading, obviously, the no-go theorems of Rozenthal and Plancherel no longer apply. Now it is definitely true that Boltzmann developed a preference towards discretizing continuous variables (although usually adding that this procedure was fictitious and purely for purposes of illustration and more easy understanding). However, there is no evidence in the (1868) and (1871b) papers that Boltzmann implicitly assumed a discrete structure of mechanical phase space or the energy-hypersurface.

Instead, the context of his (1871b) makes clear enough how he intended the hypothesis.[3] Immediately preceding the section in which the hypothesis is introduced, Boltzmann gives a clear discussion of trajectories for some simple systems: he comes back to the mass point in two dimensions with potential $V(r) = a/r + b/r^2$, that he had also studied in (1868b) and, even more simple, a two-dimensional harmonic oscillator with potential $V(x, y) = ax^2 + by^2$. In the latter case, the mass point moves through the surface of a rectangle. (Cf. Fig. 1. See also (Cercignani 1998, p. 148).) If a/b is rational, (actually: if $\sqrt{a/b}$ is rational) this motion is periodic, and Boltzmann calls x and y dependent: for each value of x only a finite number of values of y are traversed. However, if $\sqrt{a/b}$ is irrational, the trajectory will, in the course of time, traverse "almählich die ganze Fläche (Abh. I, p. 271)" of the rectangle. In this case x and y are called *independent*, since for each values of x an infinity of values for y in any interval in its range are possible. The very fact that Boltzmann considers intervals for the values of x and y of arbitrary small sizes, and stressed the distinction between rational and irrational values, indicates that he did *not* silently presuppose that phase space was essentially discrete, where

[2]Indeed, in the rare occasion in which he later did mention external disturbances, it was only to say that they are "not necessary" (Boltzmann 1895b). See also (Boltzmann 1896, §91).

[3]This has also been argued by (Brush 1976).

those distinctions would make no sense.

Now clearly, in modern language, one should say in the second case that the trajectory lies *dense* in the surface, but not that it covers it, or traverses all points. Boltzmann did not possess this language. In fact, he could not have been aware that the continuum contains more than a countable infinity of points. Thus, the correct statement that, in the case that $\sqrt{a/b}$ is irrational, the trajectory will traverse, for each value of x, an infinity of values of y within any interval however small, could easily have lead him to believe (incorrectly) that *all* values of x and y are traversed in the course of time.

It thus seems eminently plausible, by the fact that this discussion immediately precedes the formulation of the ergodic hypothesis, that the intended statement is really what the Ehrenfests called the *quasi-ergodic hypothesis*; i.e. the assumption that the trajectory lies dense (i.e. passes arbitrarily close to every point) on the energy hypersurface; or at least some hypothesis compatible with this.[4] The quasi-ergodic hypothesis is not mathematically impossible for higher-dimensional phase spaces. However, the quasi-ergodic hypothesis does not imply the desired conclusion that the only stationary probability distribution over the energy surface is micro-canonical. One might then still hope that if the system is quasi-ergodic, the only continuous stationary distribution ρ is microcanonical. But even this is fails in general (Nemytskii and Stepanov 1960).

Nevertheless, Boltzmann clearly remained skeptical about the validity of his hypothesis, or at least that it could be proven. For this reason, he attempted to explore different routes to his goal of characterizing thermal equilibrium in mechanics. Indeed, both the preceding (1871a) and his next paper (1871c) present alternative arguments, with the explicit recommendation that they avoid hypotheses. In fact, he did not return[5] to this hypothesis until the 1880's (stimulated

[4] As it happens, Boltzmann's two examples are compatible with the measure-theoretical hypothesis of 'metric transitivity' too.

[5] An exceptional occasion where the hypothesis is ergodic mentioned is a passage in the Appendix of his (1875, Abh. II, p. 29-30), where he briefly considers some system of a single two-dimensional particle and writes: "Sup-

by Maxwell's 1879 review of Boltzmann's 1868 paper.) At that time, perhaps feeling fortified by Maxwell's authority, he would express much more confidence in the ergodic hypothesis (see section 3).

3 The 1880's. Return of the ergodic hypothesis

During the 1870s, Boltzmann turned away from the ergodic hypothesis, and developed other approaches, relying on the SZA in 1872, and on the permutational argument in 1877. This latter approach introduced far-reaching conceptual shifts in the theory. Accordingly, the year 1877 is frequently seen as a watershed in Boltzmann's thinking. Concurrent with that view, one would expect his subsequent work to build on his new insights and turn away from the themes and assumptions of his earlier papers. In actual fact, however, Boltzmann's subsequent work in gas theory in the next decade and a half was predominantly concerned with technical applications of his 1872 Boltzmann equation, in particular to gas diffusion and gas friction. And when he did touch on fundamental aspects of the theory, he returned to the issues and themes raised in his 1868-1871 papers, in particular the ergodic hypothesis and the use of ensembles. Apart from two paper, i.e. (1878a, 1883), the permutational argument developed in (1877b) seems to leave no trace at all in his work until he was forcefully reminded of the reversibility objection in 1894. In this section review a selection of passages from his later work that are relevant to the the ergodic hypothesis.

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pose it were possible that [the system] could traverse all states of motion that are compatible with the principle of conservation of energy, then [certain formula's from his (1871b)] are applicable. " However, he continues: "On the other hand, if we deal with a system [...] that does not traverse all positions, velocities, and directions of velocity that are compatible with the energy principle, ...", then its characterization is not so easy. Clearly, this passage too does not indicate any confidence in the validity of the hypothesis.

3.1 1881: Boltzmann on Maxwell on Boltzmann

The next step in Boltzmann's development was again triggered by Maxwell, this time by a paper that must have pleased Boltzmann very much, since it was devoted to "Boltzmann's theorem" (Maxwell 1879) and dealt with his work of 1868.

Maxwell, characteristically, went straight to the main point of Boltzmann's 1868 paper, i.e. the theorem discussed in its last section. He pointed out that the importance of the theorem is that it does not rely on any collision assumption. But Maxwell also made some pertinent observations along the way. He is careful and critical about stating Boltzmann's ergodic hypothesis, pointing out that "it is manifest that there are cases in which this does not take place" (Maxwell 1879, p. 694). Apparently, Maxwell had not noticed that Boltzmann's later papers had also expressed similar doubts. He rejected Boltzmann'a time-average view of probability and instead preferred to interpret ρ as an ensemble density. Further, he remarks that any claim that the distribution function obtained was the unique stationary distribution "remained to be investigated (Maxwell 1879, p. 722)". Boltzmann responded by writing a presentation (1881) with the purpose of disseminating Maxwell's 1879 paper to the German-speaking physicists. (Curiously, he did not take the opportunity to comment upon those remarks of Maxwell that were critical of his own paper.) Maxwell's paper seems to have revived Boltzmann's interest in the ergodic hypothesis, which he had been avoiding for a decade, as well as to the ensemble view which never had received a central place in his thinking before.

3.2 1884-86 Monocyclic systems

Another major influence on Boltzmann's work in the 1880s were Von Helmholtz' investigations into so-called monocyclic systems. They prompted Boltzmann to explore the same subject in three papers (1884, 1885, 1886).

1884: On the properties of monocyclic systems The opening paragraph is worth quoting:

> A most complete mechanical proof of the second law would obviously consist in showing that, for every mechanical process, relations hold which are analogous to those of the theory of heat. But, on the one hand, the second law does not seem to be valid in general and, on the other hand, the properties of the so-called atoms are unknown. Therefore the problem is rather to investigate in how far there is an analogy.

This is the first occasion (to my knowledge) where Boltzmann expressed disbelief in the validity of the Second Law. It is also noteworthy how he proposes his studies as an *analogy*; rather than an attempt to provide a mechanical theorem that could be identified with the Second Law. Here we see an influence from Helmholtz which was to last for several papers (cf. Boltzmann (1887,1894)). The main difference between Boltzmann and Helmholtz is that Helmholtz had considered a purely mechanical problem, without any appeal to probability. These systems had to be stationary, as in a fluid moving through a ring-shaped channel, or, to quote Boltzmann's own example: Saturn's rings. Boltzmann noted that these conditions would also be fulfilled if we replace Helmholtz's mechanical system by a stationary ensemble.

A stationary ensemble is called a *monode* (Abh. III p.129). An ensemble for which the kinetic energy is an integrating divisor is an *orthode*. Boltzmann says, "For all orthodes equations hold which are completely analogous to thermodynamics (p. 130)." Boltzmann discusses two special cases. For an ensemble of Hamiltonian systems with coordinates $q_1, \ldots, q_g$ and momenta $p_1, \ldots, p_g$ and Hamiltonian $H(p, q) = T(p) + V(q)$, and let the number dN of such systems with p, q within certain limits be given by:

$$dN = Ne^{-hH(p,p)}dpdq$$

This type of ensemble is what he calls a *holode* (i.e., a canonical ensemble). He shows (by referring to the arguments of (Boltzmann 1871c)) that the ensemble average of the kinetic energy

$\langle T \rangle = \frac{Ng}{2h}$ is the integrating divisor of the inexact heat differential $đQ$ A holode is therefore a special case of an orthode.

Another special case is an ensemble in which no integral of motion exist but the total energy. Such an ensemble is called an *ergode*. He notes that an element of this ensemble satisfies the hypothesis of traversing every state compatible with the given total energy. Indeed, being an element of an ergode and satisfaction of the hypothesis are equivalent. (This is how the hypothesis got its name.)[6] The main result of the paper is that every ergode is an orthode.

3.3 1887: Mechanical analogies for the second law of thermodynamics

”Under all purely mechanical systems, for which equations exist that are analogous to the so-called second law of the mechanical theory of heat, those which I and Maxwell have investigated ... seem to me to be by far the most important. ... It is likely that thermal bodies in general are of this kind [i.e.: they obey the ergodic hypothesis]”

Again, Boltzmann discusses the trajectory of a mechanical system through state space, points out that the trajectory can be characterized by the integrals of the equation of motions, but that these integral equations might be satisfied for a finite number of combinations of the state

[6]The literature contains some confusion about what Boltzmann actually understood by an ergode. Brush points out correctly (in his translation of (Boltzmann 1898, p. 297) and(Brush 1976, p. 364)) that an Ergode should not be confused with an ergodic system, as used by the Ehrenfests. Indeed, an Ergode is an ensemble, not an individual system. Unfortunately, Brush construes an Ergode simply as an ensemble characterized by a particular distribution in phase space, namely the micro-canonical one (7). Thus, for him an ergode is just an micro-canonical ensemble. As we can see from the passage just quoted, this is still not correct. An Ergode is a stationary ensemble with only a single integral of motion. As a consequence, its distribution is indeed micro-canonical, but also, every member of the ensemble is an ergodic system in the sense of the Ehrenfests (i.e., it satisfies the ergodic hypothesis).

Another dispute has emerged concerning the etymology of the term ‘ergode’. The common opinion, going back at least to the Ehrenfests has always been that the word derived from ergos (work) and hodos (path). Galavotti (1994) has argued however that ”undoubtedly” it derives from ergos and eidos (similar). Now one must grant Galavotti that one would expect the etymology of the suffix “ode” of ergode to be identical to that for holode, monode, orthode and planode, and that a reference to path would be somewhat unnatural in these last four cases. However, I don’t believe a reference to eidos would be more natural. Moreover, it seems to me that if Boltzmann intended this etymology, he would have written ”ergoide” in analogy to planetoide, ellipsoide etc. The idea that he was familiar with this usage is substantiated by him coining the term “momentoide” for momentum-like degrees of freedom (i.e. those that contribute a quadratic term to the Hamiltonian) in (Boltzmann 1892). The argument mentioned by Cercignani (that Galavotti’s father is a classicist) fails to convince me in this matter.

variables or an infinity of such combinations.

To illustrate this, he again discusses the two-dimensional example shown in Fig. 1. The condition $\arcsin x = A \arcsin y$ will allow for each x a finite number of values of y, if A is rational but an infinity of values if A is irrational. (cf. fig 1.) In the latter case he calls the integrals "infinitely multivalued". The integral then "looses its meaning", and "the values of the pair x and y that are traversed now constitute a two-dimensional manifold" (ABh. III p. 262). In general, a number of the integrals might be infinitely multi-valued, and the trajectory then becomes an even higher-dimensional manifold. In the extreme case, this will be true for all integrals except the energy, and the trajectory fills the entire energy-hypersurface.

3.4 1894: Time ensembles

Another relevant paper is Boltzmann's contributions to the 1894 BAAS meeting in Oxford, which appeared as an Appendix to a paper by Bryan. It introduced a remarkable new view on ensembles:

> To express probability by means of a number we suppose the stationary state to last for a long time, Θ. Divide this time into n infinitely small parts, θ. We shall call the beginning of the first of these parts the time zero; the beginning of the second t_1, etc. After the whole time Θ has elapsed, let another series of times of length θ begin.
>
> Assume for a moment we have n separate vessels, all exactly similar to the one containing the gas; that each of these n vessels contains the same gas and that the motion of the gas is the same in each. The beginning, however is different. For example, let the gas in the second vessel at time zero be in the same condition in which the gas of the first vessel is at time t_1; in the third vessel let the gas at time zero be in exactly the same condition as it is in the first vessel at the time t_2, and so on.
>
> The probability may be defined in two ways. If we consider a single *vessel* containing gas, let τ be the fraction of the time during which the coordinates and momenta of a molecules

> lie between [certain limits], then τ/Θ is the probability required [...].
>
> On the other hand if we consider the above series of n vessels at any single *instant* of time, we can define the probability to be dz/n where dz is the number of vessels in which a molecule [has its coordinates and momenta between the given limits].
>
> We may therefore put
>
> $$\frac{\tau}{\Theta} = \frac{dz}{n}.$$
>
> (Boltzmann 1894b, Abh. III p. 520-521)

The 'first way' of defining probability mentioned here has been called a *time ensemble* by Gibbs (1902, p. 169). It is conceptually rather different from the usual one, presented here as the 'second way' of defining probability (cf. Fig. 3). The crucial point is that the question of the equality of ensemble averages and time averages is put into a very different perspective. In a time ensemble, *obviously* the time average and ensemble average are equal. (Disregarding niceties about discrete, continuous and infinite-limit averages (i.e. between $\frac{1}{\Theta}\sum_i A(t_i)$, $\frac{1}{\Theta}\int_0^\Theta A(t)dt$ and $\lim_{\Theta\longrightarrow\infty}\frac{1}{\Theta}\int_0^\Theta A(t)dt$). Yet, Boltzmann presents the two ensemble conceptions as two ways of defining the same thing, and simply equates them.

He does not note any explicit difference between his present conception and his earlier usages of ensembles, This might suggest that he understood ensembles also as time ensembles in these earlier cases. In any case, it reveals once again that Boltzmann did not rely on the ergodic hypothesis to obtain identity between these two kinds of averages, but rather hoped to obtain it by an appropriate choice of definitions.

3.5 1898 Lectures on Gas Theory II

The second volume of the *Lectures on Gas Theory* is mostly concerned with applications and contain comparatively little material on the foundation of statistical physics. However, some sections and digressions present important passages, in particular in §30,35,41 and Chapter 7.

Chapter 3 of the book develops the principles of general mechanics needed for gas theory. This is straightforward Hamiltonian mechanics. In §26 he introduces ensembles: "Just as one can represent a curve infinitely many times, each time with a different value of a parameter, so we can represent our mechanical system infinitely often so that we obtain infinitely many mechanical systems, all of the same nature and subject to the same equations of motion but with different initial conditions."

This quote is somewhat ambiguous about what kind of ensemble is intended. However, immediately subsequent to this he considers a subset of this infinite number for which the initial conditions are specified within an infinitesimal region $dp_1 \cdots dq_n$. This suggests he has an ordinary ensemble in mind. He then proceeds to discuss to investigate the case when the ensemble is stationary. Just as in the (1871) papers, he argues that a sufficient condition for stationarity is guaranteed if the distribution function depend only on the integrals of the equation of motion (which he now calls "invariants"). But in contrast to those papers he now claims that it is also sufficient. He ends the section by saying that the most simple example of such a stationary distribution is obtained when ρ is given by (7), i.e. the microcanonical distribution. He adds: I once allowed myself to call the distribution of states described by this formula [...] an ergodic one. Note that Boltzmann does not mention explicitly that his previous usage of the term 'ergodic' also assumed that there was no other integral (or invariant) than the total energy. Clearly, it is this passage that gave rise to the confusion mentioned in footnote 6.

3.6 1904: Boltzmann & Nabl

The most explicit account Boltzmann ever gave about the relation between time and particles averages is to be found in his last article on statistical physics, the Encyclopedia article co-authored with Nabl.

Let $\phi(c)dc$ represent the relative number of molecules with a velocity between c and $c + dc$,

and let the average squared velocity be

$$\langle c^2 \rangle = \frac{1}{n} \int c^2 \phi(c) dc$$

Boltzmann an Nabl write:

> The average defined here is the so-called *statistical* average, which one obtains by forming, for every molecule, at a given time, the value c^2 and taking the average of all these values. On the other hand, the *historical* average is defined by considering a single molecules during a long time t and forming the integral
>
> $$\frac{1}{t} \int_0^t c^2 dt.$$
>
> Yet, because on average all molecules behave equally, these two averages are the same for a stationary state (Boltzmann and Nabl 1904, p. 522-523).

This is the only occasion I know of in which Boltzmann recognizes that, in principle, these two types of averaging differ. And yet again, it is immediately claimed that they are equal for the stationary state. Not because if the ergodic hypothesis, but because ”all molecules behave equally”.

4 Conclusions

The first issue which any student of Boltzmann’s work must face is that of his light-hearted identification of different meanings of probability. We have seen that this is a recurrent factor in his work; from his second paper on gas theory of 1868 to his very last in 1904. How could Boltzmann have thought that these different meanings coincided?

The Ehrenfests suggested an answer: it is because Boltzmann silently or implicitly relied on the ergodic hypothesis. Indeed they showed that if one assumes this hypothesis, then equality

between different types of averages follows. Interesting as this reconstruction may be, it is clear that Boltzmann did not reason this way. He never mentioned the ergodic hypothesis as a motivation for this identification, and repeatedly expressed doubts about the validity of this hypothesis and made a point of avoiding it as much as he could. If the identification in question relied on the ergodic hypothesis, one ought assume that his distrust of the ergodic hypothesis should be accompanied by doubt about the equality of different averages. But this does not occur in Boltzmann's writing.

A (historically) more accurate explanation seems to be that Boltzmann simply believed that the interpretation of the averages or the distribution function was more or less a matter of taste which would not interfere with the mathematical results he obtained for these concepts. To be sure, this answer is not satisfactory, since this belief is wrong. But I can see no other explanation.

So what role did the ergodic hypothesis play? It seems that Boltzmann regarded the ergodic hypothesis as a special dynamical assumption that may or may not be true, depending on the nature of the system, and perhaps also on its initial state. Its role was simply to help derive a result of great generality: For any system for which the hypothesis is true, its equilibrium state is characterized by (7), which reduces in the limit $n \longrightarrow \infty$ to the Maxwell distribution, regardless of the details of the inter-particle interactions, the SZA, or indeed whether the system represented is a gas, fluid, solid or any other thermal body.

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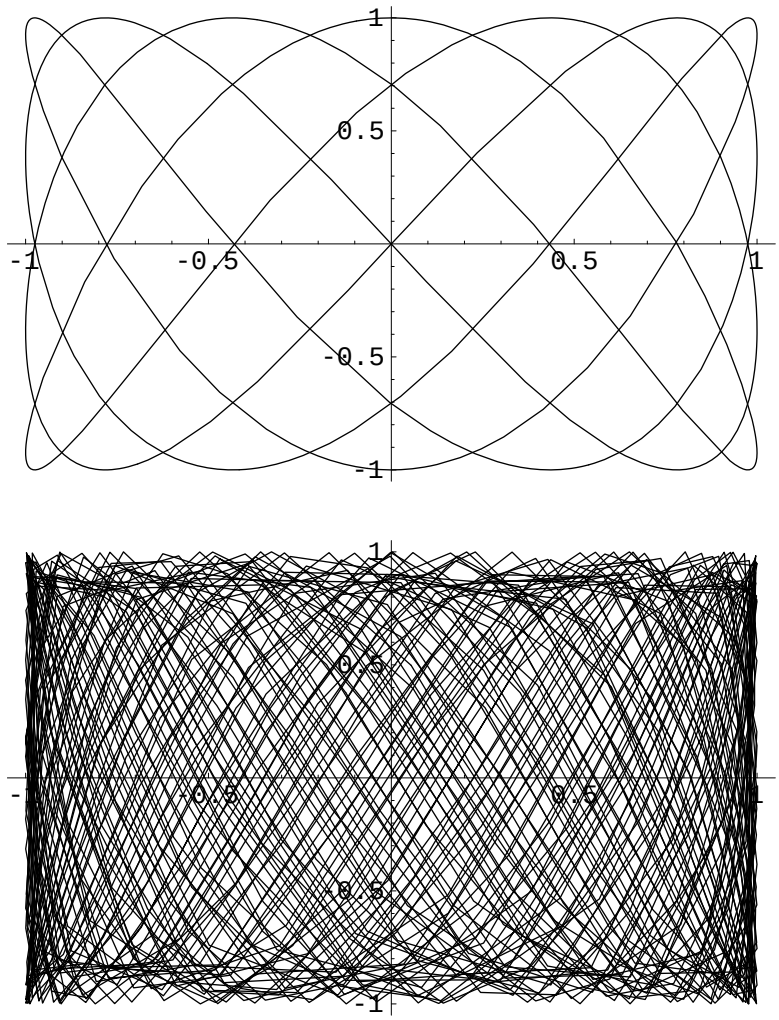

Figure 1: *The trajectory in configuration space for the potential function* $V(x, y) = ax^2 + by^2$*, illustrating the distinction between the case where (i)* $\sqrt{a/b}$ *is rational (here 4/7) and the trajectory is periodic; (ii) a fragment of the trajectory when* $\sqrt{a/b}$ *is irrational (*$1/e$*).*