"Will Someone Say Exactly what the H-Theorem Proves?" A Study of Burbury's Condition A and Maxwell's Proposition II

PENHA MARIA CARDOSO DIAS

Communicated by R. H. STUEWER

Summary

Many historians of science recognize that the outcome of the celebrated debate on BOLTZMANN's H-Theorem, which took place in the weekly scientific journal *Nature*, beginning at the end of 1894 and continuing throughout most of 1895, was the recognition of *the* statistical hypothesis in the proof of the theorem. This hypothesis is the *Stosszahlansatz* or "hypothesis about the number of collisions." During the debate, the *Stosszahlansatz* was identified with another statistical hypothesis, which appeared in Proposition II of MAXWELL's 1860 paper; BURBURY called it Condition A. Later in the debate, BRYAN gave a clear formulation of the *Stosszahlansatz*. However, the two hypotheses are *prima facie* different. BURBURY interchanged them without justification or even warning his readers. This point deserves clarification, since it touches upon subtle questions related to the foundation of the theory of heat. A careful reading of the arguments presented by BURBURY and BRYAN in their various invocations of both hypotheses can clarify this technical point. The *Stosszahlansatz* can be understood in terms of geometrical invariances of the problem of a collision between two spheres. A byproduct of my analysis is a clarification of the debate itself, which is apparently obscure.

1. Introduction

1.1 "Will someone say exactly what the H-Theorem proves?" is a famous question in the history of the theory of heat. When it was raised by EDWARD PARNALL CULVERWELL (1894a) in the weekly scientific magazine *Nature* on October 25, 1894, it generated a discussion on the meaning of BOLTZMANN's H-Theorem, which carried significant consequences for the understanding of the theory. The discussion involved CULVERWELL himself, SAMUEL HAWKSLEY BURBURY, HENRY WILLIAM WATSON, GEORGE HARTLEY BRYAN, JOSEPH LARMOR and, of course, LUDWIG BOLTZMANN. The history of the debate is well known. Briefly, it followed from the discussion that the proof of BOLTZMANN's theorem depended on a statistical hypothesis, the *Stosszahlansatz*, as it later came to be called (PAUL & TATYANA EHRENFEST). According to the hypothesis, the velocities of two molecules of, say, a perfect gas are statistically independent, even when the molecules are about to collide. Actually, this hypothesis first arose in RUDOLF JULIUS EMMANUEL CLAUSIUS's epoch-making 1858 paper on the mean free path, although he stated it for a particular and unrealistic situation.[1] In 1860, JAMES CLERK MAXWELL wrote a complete expression for the *Stosszahlansatz*, which, in 1866, became a starting point for his second proof of the distribution of velocities.[2] Furthermore, the debate took place long after BOLTZMANN's answer to LOSCHMIDT (BOLTZMANN, 1877). Some historians of science (MARTIN J. KLEIN; STEPHEN G. BRUSH, 1976) have therefore proposed that what occurred in 1894–1895 was the recognition of the *Stosszahlansatz* as an independent hypothesis in the proof of the H-Theorem, or, according to BRUSH (1976, vol. 2, p. 620), the identification of "the stage in the proof . . . where irreversibility sneaks in."[3]

1.2 However, initially BURBURY associated the proof of BOLTZMANN's theorem with a well-known proposition, which entered the theory as Proposition II in MAXWELL's paper of 1860. This proposition involves a statistical postulate to which BURBURY gave the name Condition A. Briefly, according to Condition A, when two spherical molecules collide, for any given direction of the incoming relative velocity, the position of the impact parameter is uniformly distributed over all of the possible values it can have. Still during the debate, BURBURY – and BRYAN after him – substituted the *Stosszahlansatz* for Condition A;

---

[1] CLAUSIUS considered that all the molecules but one were at rest. He then calculated the probability that this single molecule would collide with any one of the molecules at rest.

[2] In 1860 MAXWELL proved the law of velocities, supposing that the three components were statistically independent. He realized, however, that there were not enough grounds for this supposition, and he tried a new proof in 1866 that did not involve this assumption.

[3] Historically speaking, BRUSH's remark is correct. It need not be so from the physical point of view. It has been noticed (HAROLD GRAD, C. CERCIGNANI, OSCAR E. LANFORD III) that irreversibility appears when, in the proof of the H-Theorem, appropriate limits are taken, rather than in the factorization. Letting σ be the diameter of the molecules, m be the mass of each molecule and N be the total number of molecules, the limit is the following:

$$\sigma \to 0 \quad m \to 0 \quad N \to \infty$$

and

$$N\sigma^2 \to \mathit{finite}\ (\neq 0) \quad Nm \to \mathit{finite}\ (\neq 0) \quad N\sigma^3 \to 0;$$

in this limit, the mean free path ($\propto (N\sigma^2)^{-1}$) is non-null, but the volume occupied by the molecules ($\propto N\sigma^3$) vanishes. However, it is true that the *Stosszahlansatz* is time asymmetric.

actually, he meant an equivalence between the two hypotheses. The mere interchange of hypotheses is known to historians; it was noticed, for example, by THOMAS S. KUHN (1978). However, the issue deserves more attention than has been given to it.

In his paper of 1858, CLAUSIUS treated molecular collisions as statistical events; furthermore, these random collisions were the mechanism that explained the phenomenon of the (irreversible) diffusion of gases. Proposition II, because of its Condition A, shows *how* collisions can function as a randomizing mechanism (MAXWELL, 1860). Condition A refers to the possible ways in which two molecules can collide. The *Stosszahlansatz* is *prima facie* a different hypothesis. It is an abstract general probabilistic assumption on the joint occurrence of two probabilistic events; it is the very definition of statistical independence applied to the velocity states of two molecules when they are about to collide. Condition A, although statistical, has a simple geometrical interpretation. The *Stosszahlansatz* is counter-intuitive: whether two molecules collide or not depends on their trajectories, hence on the equations of motion, not on probabilities.

Now, if the equivalence of the hypotheses can be proved, then the *Stosszahlansatz* acquires a geometrical interpretation that bears upon the nature of the molecular motion. Consequently, the basis on which the interchange of hypotheses was made involves an issue of both historical and conceptual significance.

1.3 BURBURY interchanged the hypotheses without providing a justification and without warning his readers that he did it. Furthermore, only once in his papers prior to the debate in *Nature* did BURBURY give an interpretation of the *Stosszahlansatz*, which was similar to the one it would have after the identification of the hypotheses during the debate; but this earlier interpretation lacks a context that calls attention to the identification of two apparently different hypotheses. In other papers, BURBURY used the two hypotheses independently; he also did so in his first two letters to *Nature*, of November 22, and December 20, 1894.

I therefore shall analyse BURBURY's and BRYAN's arguments as presented in the debate in *Nature* and their uses of Proposition II and of the *Stosszahlansatz* in other publications, to see how an equivalence between the propositions can be proved. A clarification of their arguments certainly gives a meaning to the *Stosszahlansatz*, even if limited and restricted to a specific system, that of a perfect gas made of identical spherical molecules.

I start with a general section (Section 2), in which I state the problem in detail, placing it in its historical context. Although BURBURY interchanged hypotheses, it was BRYAN who gave the best statement of the *Stosszahlansatz*, during the debate; but he learned about it from BURBURY, as he conceded. In Section 3, I analyse BRYAN's explanation of what BURBURY taught him. In Section 4, I analyse BURBURY's various uses of Condition A and of the *Stosszahlansatz*. It might be said that the *Stosszahlansatz*, as it stood in 1894–1895, was a statistical hypothesis that had a meaning in terms of certain geometrical invariances of the problem of a collision between two spheres. I add an

Appendix that is not historical, but will help in following the argument. A by-product of this paper is a clarification of the debate in *Nature*, which is otherwise difficult to understand.

2. Burbury's Condition A

2.1 In his letter of October 25, 1894, to *Nature*, CULVERWELL (1894a) revived the paradox of J. J. LOSCHMIDT in order to criticize the proof of the H-Theorem that was given by H. W. WATSON (1893) in the recently published second edition of his book on the kinetic theory of gases. Briefly, LOSCHMIDT found an inconsistency between the laws of mechanics and the existence of a functional, H, that decreases *monotonically* in time: According to the laws of mechanics, for each trajectory in phase space for which H decreases, there is another trajectory for which H increases, which is obtained from the former by reversing, at a particular instant, the signs of the velocities of all the molecules in the gas. How BOLTZMANN escaped the paradox is well known, and can be found in the literature (KLEIN, 1973). I only note KLEIN's remark that by 1894 physicists should have known that the H-Theorem is statistical and hence that LOSCHMIDT's criticism was not applicable. It should be added, following BRUSH's remark already quoted in the introduction, that CULVERWELL apparently did not criticize the content of the theorem, as LOSCHMIDT did. Rather, he criticized the particular proof given by WATSON, which according to him did not appear to be statistical (CULVERWELL, 1895b):

> I found it hard to conceive how any proof on the line of Dr. Watson could be valid *because that proof appeared to me to be a purely dynamical proof*, and I applied the reversibility argument to *show that a purely dynamical proof was impossible*, so that the H-theorem could not be a purely dynamical theorem; and after indicating the lines on which it appeared that there might be an *average dynamical* theorem, I asked if some one would say what the H-theorem really was.

2.2 The first person to address CULVERWELL's challenge was BURBURY (1894a), in a letter published in *Nature* on November 22, 1894. The central point of BURBURY's argument was that the proof of the H-Theorem depended on a certain Condition A. If we imagine that the molecules are spherical bodies, a collision between two of them occurs when the center of one of the spheres is on the so-called "collision sphere." This is a spherical surface concentric with one of the molecules, and of radius σ, which is equal to the sum of the radii of the two spheres (Fig. 1). The "collision coordinates" are the spherical coordinates φ and θ, defining the position of the center of the approaching molecule on the collision sphere (Fig. 2). The coordinate φ defines the plane containing the line joining the centers of the two molecules at collision and the incoming relative velocity; the coordinate θ is in this plane and is the angle between

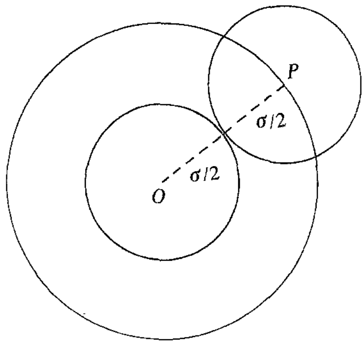

Figure 1. Two identical, spherical molecules are colliding. The "collision sphere" is the sphere of radius $OP = \sigma$, equal to the molecular diameter, and center at O, the center of one of the molecules. The center of the other molecule must be at a point P, on the "collision sphere."

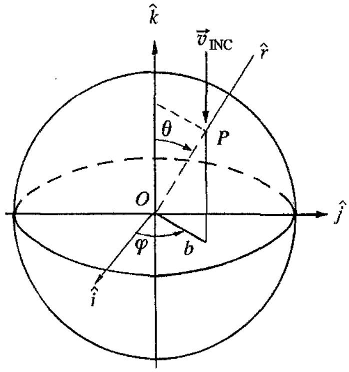

Figure 2. The "collision coordinates" are the coordinates θ and φ, which are the coordinates – on the collision sphere – of the center, P, of the approaching molecule. The incoming relative velocity, $\vec{v}_{\mathrm{INC}}$, is a vector through P. The impact parameter, b, is the distance from the center of the molecule at rest at O to $\vec{v}_{\mathrm{INC}}$; for any arbitrary motion of the molecules, it is defined as the distance between the directions of motion of the two spheres.

the incoming velocity and the line joining their centers. Or, as BURBURY put it (1894a):

> The point in which a line parallel to the relative velocity through the center of one sphere cuts a circular area of radius [σ], drawn through the centre of the other sphere at right angles to that line . . . .

The coordinates $b = \sigma \sin\theta$ and φ define, respectively, the impact parameter and its direction on the plane (x, y). When two spheres collide *elastically*, the

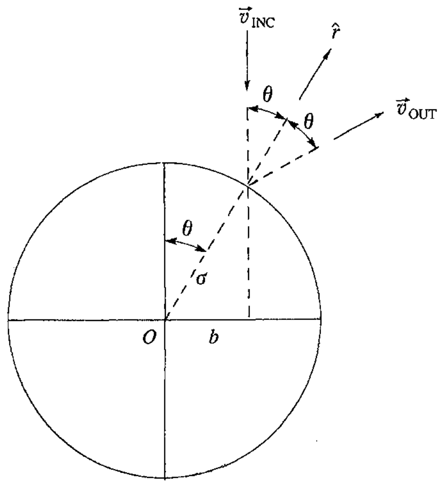

Figure 3. The result of an elastic collision is to change the relative velocity from $\vec{v}_{INC}$ to $\vec{v}_{OUT}$, $|\vec{v}_{INC}| = |\vec{v}_{OUT}|$; 2θ is the angle of scattering. According to Maxwell's Proposition II (Section 2.3), if it is assumed that "every position [of b on the great circle perpendicular to $\vec{v}_{INC}$] is equally probable," then all directions of scattering are equally probable.

collision only changes the direction of the relative velocity, in such a way that the angle between the outgoing direction and the line joining their centers is still θ, the same as the angle between the line and the incoming velocity (Fig. 3). With these remarks, it is possible to formulate Condition A and a proposition that results from it. According to BURBURY (1894a):

> If the collision coordinates be taken at random, then the following condition holds, *viz.*: – For any given direction of [the relative velocity] R before collision, all directions after collision are equally probable. Call that condition A.

BURBURY's answer to CULVERWELL consisted in claiming that Condition A need not be true for the reversed motion, so that one of the premises of the theorem having failed, the conclusion did not necessarily follow.

2.3 The assertion that the equal probability of all possible positions of the impact parameter on the plane perpendicular to the incoming relative velocity implied the equal probability of all possible directions of scattering appeared as Proposition II in MAXWELL's first paper on kinetic theory (MAXWELL, 1860, p. 379):

> To find the probability of the directions of the velocity after impact lying between given limits.

To prove this proposition, MAXWELL made a statistical assumption: On the great circle of the collision sphere perpendicular to the incoming velocity "every position [of the impact parameter] is equally probable" (1860, p. 379). *This is Condition* A, of course. With it, the probability of finding the impact parameter with length between b and $b + db$ and direction between φ and $\varphi + d\varphi$ is $\frac{b\,db\,d\varphi}{\pi\sigma^2}$ (see Fig. 3), which is equal to $\frac{\sigma^2}{4\pi\sigma^2}\sin(2\theta)\,d(2\theta)$. Since 2θ is the angle between the incoming and outgoing velocities, this result can be paraphrased by saying that all directions of scattering are equally probable.

2.4 MAXWELL (1860) invoked Proposition II to show how collisions randomized the directions of motion of the molecules, bringing about isotropy of pressure, as demanded by the equation of state for perfect gases. In this use, Proposition II becomes a kind of "proof" of how equilibrium of pressure (transmission of linear momentum) sets in, and thus is, metaphorically speaking, a sort of H-Theorem. As for CLAUSIUS (1862), he used Proposition II to illustrate that the theory of heat was concerned only with "irregular" motions, and therefore that all "non-irregular" motions have to be excluded from the beginning. The "non-irregular" motions in question were those of a row of equal spheres constrained to collide only through head-on collisions. Of course, the effect of each "non-irregular" collision is to move the target sphere forward, along a row to the position of the next sphere, so that the net effect is a forward shift of the row as a whole; the transmission of matter, energy, and momentum, being along a row, is not isotropic, and this system never reaches thermodynamic equilibrium. CLAUSIUS (1862) also gave an insightful reading of Proposition II for, according to him, it showed that the motions before and after collision had an "independent component" – the relative velocity – and a "dependent component" – the velocity of the center-of-mass, which is invariant, owing to the conservation of momentum.

2.5 CULVERWELL was not convinced by BURBURY's answer. In a letter of November 29, 1894, to *Nature* (1894b), he claimed that BURBURY's answer only showed that:

> [E]ven for the simple case of perfectly hard and elastic spheres, some amount of assumption as to an average state having been already attained must be made . . . .

Furthermore, he added, Proposition II was not general enough (1894b):

> [I]f [Mr. BURBURY] can say what assumption in a generalized system will replace the assumption of equal distribution of velocities in different direction[s] in a system of hard spheres, he will clear up the whole difficulty.

Thus, BURBURY, when responding in a letter to *Nature* on December 20, 1894 (1894b, p. 175), tried:

> to extend the proof of the H-theorem which I gave for elastic spheres to a more general, but not the most general case.

However, except for the use of generalized momenta and coordinates, there seems to be no substantial difference between his statement of Condition A in this letter and in his earlier one (BURBURY, 1894b, p. 175):

> I will now assume (condition A) that the coordinates θ' [φ'] are taken at haphazard without regard to the variables $P'q'$ [of phase space, after discounting the collision coordinates].

However, when BURBURY wrote another letter to *Nature* on January 31, 1895, Condition A was not the former hypothesis, but definitely the *Stosszahlansatz* (1895a):

> The initial distribution of R, the relative velocity, *i.e.* the number of pairs of spheres for which it has given direction is arbitrary – condition A is fulfilled.

That is to say, BURBURY seems to be introducing a new Condition A: The number of pairs of spheres for which the relative velocity, before collision, has a given direction is "arbitrary." This number was defined in previous uses as follows (BURBURY, 1894a, p. 78):

> $Ff\,dS$ is the number of pairs whose relative velocity R falls within the cone described with solid angle dS about [R] as axis.

Thus "arbitrary" stands for the factorized distribution $Ff\,dS$, and the new Condition A is the *Stosszahlansatz*. From this new Condition A, BURBURY inferred Proposition II (1895a):

> Then, as proved, whatever the initial distribution, after collision, the distribution of R is uniform, *i.e.* all directions [are] equally probable.

Consequently, the assumption that the collision coordinates are "taken a[s] haphazard" (the original Condition A) has been replaced in Proposition II, by the *Stosszahlansatz*; this supports the view that BURBURY meant to use the two hypotheses equivalently.

3. What Bryan Learned from Burbury

3.1 Although BURBURY introduced the *Stosszahlansatz* as an independent hypothesis, its clearest statement during the debate was given by BRYAN (1895), in a letter published in *Nature* on May 9, 1895. It seems that BOLTZMANN's intervention in the debate with his emphasis on the statistical nature of the theorem, and CULVERWELL's agreement, which followed, brought some order to the debate and clarified CULVERWELL's quest. BRYAN thus was ready to summarize matters (1895, p. 29):

> What we want to know is what assumptions are involved in the mathematical proofs of the theorem, why they have to be made, and for what systems they are likely to hold. This question has been ably treated by Mr. Burbury, but in view of Prof. Boltzmann's assertion that the theorem is one of

probability, it is desirable to examine more fully where probability considerations enter into proofs such as Dr. Watson's, which contain no explicit reference to them.

He could now answer CULVERWELL and state a hypothesis that is true even for generalized systems (BRYAN, 1895, p. 29):

It is then necessary to assume that *the probabilities for the two kinds of molecules are independent of each other.*

3.2 Having stated the *Stosszahlansatz*, BRYAN made, however, a curious remark (1895b, p. 29):

This assumption was pointed out to me by Mr. Burbury and is what I intend[ed] to imply in my previous letter when I said that Dr. Watson's assumption was more *natural* than any other. Under these circumstances alone can we assert that the probability of a given combination of coordinates and momenta of *two* molecules is proportional to $F\,dP_1 \ldots dQ_n \times f\ dp_1 \ldots dq_n$.

Actually, he learned this assumption from BURBURY, long before the debate in *Nature*; to wit, he had already learned it by August 9, 1894.

The British Association for the Advancement of Science asked BRYAN and LARMOR to write a report on the "state of knowledge" of Thermodynamics and its Second Law (BRUSH, 1976, vol. 2). The first Report (BRYAN, 1891) was read on August 20, 1891, at the Association's meeting held at Cardiff. The second Report (BRYAN, 1894a) was read on August 9, 1894, at the Association's meeting held at Oxford; in this Report, BRYAN presented two unambiguous formulations of the *Stosszahlansatz*.

In the first Report, BRYAN discussed earlier attempts to derive the macroscopic Second Law from dynamical principles; he also discussed MAXWELL's 1860 method of deriving macroscopic properties from collisions that are statistical events. The H-Theorem was not discussed.

BRYAN's second Report (1894a, p. 64) "deals primarily with Boltzmann-Maxwell Law and Maxwell's Law of Partition of Kinetic Energy, which form the basis of the Kinetic Theory of Gases." Here, he stated the *Stosszahlansatz* twice. The first statement is unambiguous, but not the most illuminating one (BRYAN, 1894a, pp. 77–78):

[If the distribution] is a function of the energy alone it must be of the well-known form

$$e^{-kE}.$$

For before two molecules encounter each other the frequency of distribution of the coordinates and momenta of one cannot depend on the coordinates and momenta of the other. Hence if f_1, f_2 denote the frequencies of distribution of the two molecules just before the encounter

$$f_1 \times f_2 = f(E)\,.$$

BRYAN's second statement of the *Stosszahlansatz* is illuminating on at least two counts:

(i) it is a written testimony of what BURBURY told him.

(ii) it gives an interpretation of the *Stosszahlansatz* in terms of the undetermination of the mechanical problem of molecular collisions, which is the main point of BRYAN's intervention in the debate in *Nature* (BRYAN, 1894a, pp. 83–84):

> The assumptions involved in proving the Boltzmann-Maxwell Law for colliding bodies seem to me to resolve themselves into the following: . . . That any molecule has a chance of colliding with any other molecule. Hence the frequency of distribution of the molecules must depend on their actual state, and not on their past history or future prospects of colliding with any particular set of other molecules. As Burbury has just written in a letter to me: "To take conventional elastic spheres as the simplest case we always assume as fundamental that if $f(a)$ denotes the chance of sphere A having velocity a, and $f(b)$ the chance of sphere B having velocity b, then *the chances are always independent*, whether A and B collide or not."

3.3 BRYAN began his first letter to *Nature* of December 5, 1894 (1894b), by noting that by applying the test of reversing velocities at each separate stage of the proof of the H-Theorem, it should be possible to discover any assumption on irreversibility that might be hidden in the proof. He thus proposed to apply this test to the following assumption made by WATSON (1898, p. 43):

> [T]he expression $Ff\ dP_1 \ldots dq_{n-1}\dot{q}_n$ is the number of pairs of molecules, one from each of these sets, passing from the state $P, P + dP \ldots q, q + dq$ to the state $P', P' + dP' \ldots q', q' + dq'$ per unit of time, where $\dot{q}_n$ is put equal to 0 in f.[4]

BRYAN reasoned that if the motion were irreversible, then upon reversal of the velocities the number of pairs of spheres passing from an "accented" state (the two-molecule state just before collision, in the reversed motion) to an "unaccented" state (the two-molecule state just after collision, in the reversed motion), through a (reversed) collision, could not be $FfdP_1 \ldots dq_{n-1}\dot{q}$, as in the direct motion. He justified this contention as follows (1894b):

> [T]his number will depend on F and f, *the frequencies of distribution which the molecules are about to have after the collisions have taken place.*

The point is that an irreversible motion was unpredictable (1894b):

> [I]f Mr. Culverwell endows his molecules with the power of forethought and the prediction regarding their future state necessary to enable them

[4] The restriction $\dot{q}_n = 0$ means that the molecules are colliding. For instance, it corresponds to making the distance between the centers equal to σ, the diameter of the molecules.

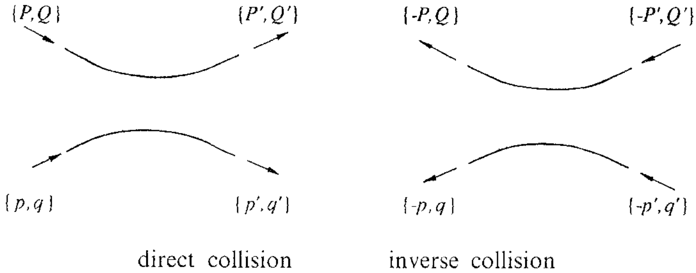

Figure 4. The trajectories of the molecules in the "direct" and "reversed" collisions are identical, but the momenta have different signs.

> to regulate their movements according to this suppositious law [the law $Ff\ dP_1 \ldots dq_{n-1}\dot{q}_n$], then Dr. Watson's proof, and indeed any proof, will necessarily fall to the ground.

3.4 In fact, if the motion is reversible, then, upon reversal, a collision reproduces the initial state of the direct collision, except for the signs of the velocities, which are reversed. Clearly, the number of pairs of molecules making a transition between two such states of reversed velocities is equal to the number of pairs making the corresponding direct collision, or passing from a state belonging to the phase space volume $P, P + dP, \ldots, q, q + dq$ to a state belonging to the phase space volume $P', P' + dP', \ldots, q', q' + dq'$ (which is $Ff dP_1 \ldots dq_{n-1}\dot{q}_n$, according to WATSON's assumption). Furthermore, and more important, in a reversible motion the result of a collision is uniquely determined given the initial conditions, and conversely, so that the number of pairs in the initial state is not only equal to the number of pairs in the final state, but predictability also can be paraphrased by saying, as BRYAN did, that the number of pairs in the initial state depends upon the final state.

However, if the reversed motion is also unpredictable, then it need not reproduce the same states of the direct collision with reversed velocities, so that the number of pairs in the "accented" state need not be $Ff\, dP_1 \ldots dq_{n-1}\dot{q}_n$; nor is it a function of the final, "unaccented" state, according to BRYAN's reasoning.

BRYAN then gave an illustration of a collision leading to unpredictable results. After BURBURY invoked Proposition II in his letter of November 22, 1894 (1894a), it comes as no surprise that what followed was a conspicuous allusion to Proposition II (BRYAN, 1894b):

> What Mr. Culverwell's objection shows, then, is that it is possible to conceive the molecules of a gas so projected that they would not tend to assume the Boltzmann-Maxwell distribution.
>
> But practically it would be impossible to project the molecules in their reversed motions with sufficient accuracy to enable them to retrace their steps for more than a very few collisions, just as, if we try placing a number of pool balls in a straight line on a billiard table at distances of a foot or

two apart, we find it impossible to project the first ball with sufficient accuracy for each ball to strike the next in front all down the line if there are many balls.

3.5 If BRYAN succeeded in identifying the hypothesis in the theorem that failed the test of reversing velocities, he did not seem to pay any attention to the factorization of the "number of pairs" for the direct unpredictable motion, $Ff\,dP_1 \ldots dq_{n-1}\dot{q}_n$. Even less clear was his choice for the "number of pairs" in the reversed motion if it had to be unpredictable, or his choice of a function of the initial, "accented" state (BRYAN, 1894b):

If however the motions of the molecules are allowed to take their own natural course, and nothing special is known about them, the only reasonable assumption to make is that the number of pairs passing from the accented to the unaccented state per unit of time is $F'f'\,dp'_1 \ldots dq'_{n-1}\dot{q}'_n$.

That is to say, BRYAN left unexplained what the assumptions $Ff\,dP_1 \ldots dq_{n-1}\dot{q}_n$, for the direct irreversible motion, and $F'f'\,dP'_1 \ldots dq'_{n-1}\dot{q}'_n$, for the reversed irreversible motion, had to do with the unpredictability of the motion, given his characterization of an unpredictable motion as one in which the molecules collided according to Condition A and Proposition II. In addition, recalling his letter of May 9, 1895, cited at the beginning of Section 3.2, he did not explain why "Dr. WATSON's assumption" – the factorized, "accented" distribution – was "more natural than any other." No wonder that CULVERWELL did not understand BRYAN's argument, and that his answer of January 10, 1895, was ironical and directly to the point (CULVERWELL, 1895a):

Mr. Bryan thinks that a condition which excludes the reversed motion is implied in Dr. Watson's proof, for he says that in taking unaccented letters Ff as proportional to the number of molecules passing from one configuration to another in the reversed motion, I make a less "natural" supposition than Dr. Watson, who takes accented letters $F'f'$. I cannot see what virtue there is in putting accents on or leaving them off . . . . What we want is a *proof* that the collisions will make H decrease, and we can hardly be satisfied with a proof which depends on the previous assumption that the particles do "naturally" tend to move in the desired way.

3.6 However, in his letter of May 9, 1895, BRYAN (1895, pp. 29–30) interpreted further his considerations of December 20, 1894:

If we were to reverse the motion exactly, we should have one in which the probabilities for two molecules before an encounter were not independent, and our assumption (*however improbable*) would be therefore entirely based on our previous experience with the direct motion . . . . This is what I intended to imply in my previous letter; but as I had used accented and unaccented letters in my statement, I failed to make my meaning clear to Mr. Culverwell, who evidently found it difficult to understand a proof involving their use.

The content of BRYAN's considerations of December 20, 1894, is that the motion can only be *exactly* reversed if, after the collision has *actually* occurred, the collision coordinates (φ, θ) become determined. The solution of the problem of a collision between two spheres is outlined in the Appendix. It can be seen that knowledge of φ and θ, together with knowledge of the azimuthal coordinate ($\Psi = \pi$, in Fig. 3; or Ψ, in Fig. 5 below) for the incoming velocity in *absolute* space (the incoming velocity is, say, parallel to "the vertical") restores determinism to the problem. The point is that now the (relative) velocity of the scattered spheres becomes uniquely determined by the incoming velocity, and conversely (see the expressions for $\vec{v}_{\mathrm{INC}}$ and $\vec{v}_{\mathrm{OUT}}$ in the Appendix). And once the relative motion is completely known, it suffices to give the velocity of one of the molecules to fix uniquely the velocity of the other. Perhaps this is what BRYAN meant when he observed that (1895) "it will be seen that the probabilities for two molecules are not independent of each other *after* a collision between them."

3.7 If this were all there is to say about statistical correlations, it could be said that their absence is associated with incomplete knowledge of the incoming relative velocity. These are, however, mechanical considerations, and in principle they need not be related to statistical considerations, although nothing forbids a mechanical property being used as a guide in assigning probabilities. For instance, to give a classical example, the assumption that the phase space trajectory of a classical gas in thermodynamic equilibrium is dense on the energy surface has been used to justify the microcanonical distribution insofar as it gives a rational support to the assignment of equal probabilities to equal areas on the energy surface. It is thus convenient at this point to examine what statistics itself has to say about lack of knowledge of the "collision coordinates" and about inferring statistical independence of the velocities from Condition A, and possibly the converse as well. In my view, BRYAN's understanding of what BURBURY told him, and BURBURY's various statements of Condition A reveal the associations he made between this hypothesis and the more general *Stosszahlansatz*.

4. Condition A Becomes the Stosszahlansatz

4.1 In his letters of November 22 and December 20, 1894, BURBURY (1894a and b) invoked Proposition II to write the number of pairs that reached given states after collision. In the proof of the H-Theorem, this is the so-called number of "restitutive" collisions. At any instant, there is a number of molecules leaving given states after they collide, and a number of molecules reaching these same states after a collision, the difference between these numbers giving the time variation of the distribution, which is used to prove that H decreases. In his letter of November 22, BURBURY thus stated (1894a):

> The number which after the collisions belong to the class $Ff\,dS$ will be on the above assumption [Condition A] $\frac{dS}{4\pi} \iint F'f'\,dS'$,

where dS is the area subtended by the solid angle described by the incoming relative velocity in velocity space. In his letter of December 20, BURBURY stated (1894b, p. 175):

> I will now assume (condition A) that the coordinates $\theta'\phi'$ [my $\theta'\varphi'$] are taken at haphazard without regard to the variables $P'q'$; if that be so, the chance that, for given $P'q'$, before encounter, the pair of molecules shall be in the $Pq\theta\phi$ [my $Pq\theta\varphi$] state after encounter is $\dfrac{d\theta\, d\phi'}{4\pi}$ [my $d\theta\, d\varphi'$],

where $p'q'$ is the set of canonical coordinates of one of the molecules, excluding the "collision coordinates" (φ, θ), and $P'Q'$ is the same set for the other molecule.

Continuing his reasoning, BURBURY missed on both occasions, however, a good opportunity to call attention to the *Stosszahlansatz* as an independent assumption in the proof, as well its relationship to Condition A. On the contrary, BURBURY introduced the factorized distribution as if he had nothing to say about it, and as if it had nothing to do with his Condition A. Returning now to BURBURY's letter of November 22, he introduced the *Stosszahlansatz* as follows (1894a):

> But, before the collisions [the number of pairs with relative velocity in dS] is $Ff\,dS$. Therefore, as the result of collisions it is increased by $dS\left(\dfrac{\iint F'f'\,dS'}{4\pi} - Ff\right)$.

And in his letter of December 20, he introduced the *Stosszahlansatz* as follows (1894b, p. 175):

> But the number of pairs which now are in the state $P'q'$ is $F'f'\,dP' \ldots dq'$. And therefore the number which after encounter will be in the state $Pq\theta\phi$ [my $Pq\theta\varphi$], having passed thereto from the state $P'q'$, will be $F'f'\ dP'\ dQ'\ dp'\ dq'\ \dfrac{d\theta'\, d\phi'}{4\pi}$ [my $\mathrm{d}\theta'\ d\varphi'$] ....

4.2 Prior to the debate in *Nature*, BURBURY published three papers (1886, 1890 and 1892) and an abstract of the 1892 paper (1891), where he presented proofs of the H-Theorem.

The paper of 1892 contains a general treatment of collisions, using generalized coordinates. The proof of the H-Theorem is similar to BOLTZMANN's proof; no reference is made to Proposition II and its Condition A. The papers of 1886 and 1890 are close to BURBURY's first two letters to *Nature*. In those papers, equilibrium is better described by the following consequence of the MAXWELL-BOLTZMANN distribution (1890, p. 299):

> In Maxwell's distribution, if we consider all pairs of molecules, M and m, having common velocity V, and relative velocity $R + r$, for given V all directions of R or r are equally probable.

Then, Burbury proves that a distribution for which all directions of the relative velocity are equally probable (for any given direction of the center-of-mass) is undisturbed by collisions, and conversely (1890, p. 299):

> (a) Every distribution of velocities among the molecules which satisfies the condition that for given [velocity of the center-of-mass] V all directions of [the relative velocity] R are equally probable, is undisturbed by encounters ... and is therefore ... stationary.
> (b) No distribution whatever of velocities among the molecules is undisturbed by encounters ... unless it satisfies the condition that for given V all directions of R are equally probable.

Part (a) corresponds to the stationary character of the Maxwell-Boltzmann distribution; part (b) is Burbury's version of the H-Theorem. This conception of the approach to equilibrium emphasizes the role of Proposition II as the mechanism of randomization of the direction of motion of the molecules. No wonder that Condition A was immediately invoked by Burbury when he first answered Culverwell. Analogously to the letters of November 22 and December 20, Proposition II gives the fraction of the total number of pairs of molecules whose relative velocity falls within the solid angle dS' after scattering. However, Burbury used Condition A and the *Stosszahlansatz* as if they were independent hypotheses. As for the *Stosszahlansatz*, in 1886 it was applied to the Maxwell-Boltzmann distribution; this application begs the question, since the Gaussian distribution is good only for statistically independent events. In 1892, the *Stosszahlansatz* was defined independently of Condition A (1892, p. 415):

> The number of pairs of systems, each consisting of one system from each set, whose coordinates and velocities at any instant lie within the above limits, is $dp_1 \ldots d\dot{p}_1\, dp_{r+1} \ldots d\dot{p}_n Ff$.

The same is true of the 1891 abstract (p. 177):

> And $FfR\, dp_1 \ldots dv_{n-1}$ denotes the number in unit of time of collisions between members of the two sets having their coordinates $p_1 \ldots p_{n-1}$ and velocities $v_1 \ldots v_n$.

However, in 1890, Burbury gave the following definition of the *Stosszahlansatz* (p. 301):

> Now $F_p f_p$ represents the chance that, given [the velocity of the center-of-mass] $V = OC$, the relative velocity shall have direction PCp.

That is to say, *the factorized distribution is the distribution of the relative velocity.*

If this definition makes sense, then after collision the *Stosszahlansatz* is a consequence of Condition A, according to Proposition II. But Burbury meant an equivalence between hypotheses, as can be seen by the use he made of the *Stosszahlansatz*, in his proof of part (a) of the theorem quoted above. Initially, he wrote the number of pairs, which leaves a state of relative velocity with direction in dS, and the number of pairs, which reaches this state coming from dS', as respectively proportional to $F_P f_p \frac{dS\,dS'}{4\pi}$ and $F_{P'} f_{p'} \frac{dS\,dS'}{4\pi}$; then BURBURY argued that if $F_P f_p = F_{P'} f_{p'}$, then (1890, p. 301) "the distribution of velocities is not affected by encounters. So (a) is proved," since the *Stosszahlansatz*, according to the above definition, is the distribution of the relative velocity.

4.3 The point of BURBURY's various uses of Condition A, quoted in Section 4.1, is that Condition A gives "the chance that, for given $P'q'$, before encounter, the pair of molecules shall be in the $Pq[\varphi]$ state after encounter," so that when distributing φ, b (or θ) according to Condition A, or according to any other law for that matter, the initial states $P'q'$ should be considered to be known. In Section 4.2, it was shown that BURBURY (1890) defined the factorized distribution as the distribution of the relative velocity. And BRYAN (Section 3.6) associated the *Stosszahlansatz* with incomplete knowledge of the "collision coordinates," which implies incomplete knowledge of the incoming relative velocity. Since what is involved in the *Stosszahlansatz* is the statistical independence between the velocities of two molecules when they are "about to collide," it is convenient at this point to delineate the information that needs to be given, in order to formulate the mechanical problem of molecular collision. The needed information is:

I_1: There is a molecule at rest at the origin of coordinates.

I_2: This molecule is colliding with another molecule. I_2 need not say more than that the center of the moving sphere is on the collision sphere. This imposes constraints on the mechanical problem, because the incoming velocity and the line joining the centers of the molecules belong to the same great circle of the collision sphere, which is defined by φ. It is thus convenient to include in I_2 all of the information giving meaning to the variables φ, θ, and $b = \sigma \sin\theta$. I_2 might even say that b is defined on the great circle perpendicular to the incoming velocity, without specifying which great circle it is or the direction of the velocity. Clearly, I_2 gives the range of φ, θ, and b; I_2 might include a definition of the collision sphere.

I_3: The direction of the incoming (relative) velocity in absolute space, its azimuthal direction (Ψ).

I_4: The magnitude of the relative velocity.

Condition A seems to give the (joint) distribution of φ and b (or of $b = \sigma \sin\theta$) based upon knowledge of I_1, I_2, I_3, and I_4. It says that this distribution is $\frac{\sigma^2 b\, db\, d\varphi}{\pi\sigma^2}$ or $\frac{\sigma^2 \sin(2\theta)\, d(2\theta)\, d\varphi}{4\pi\sigma^2}$, a number that is independent of I_3 and I_4 but depends on b (or θ), I_2 (which characterises the variables φ, b at collision), and I_1. The reason I_1 seems to be pertinent to the distribution of φ, b, is that these variables are defined with respect to the center of a molecule at rest, not with respect to an arbitrary origin in space. Otherwise the problem loses its meaning as one involving the scattering of one molecule by another,

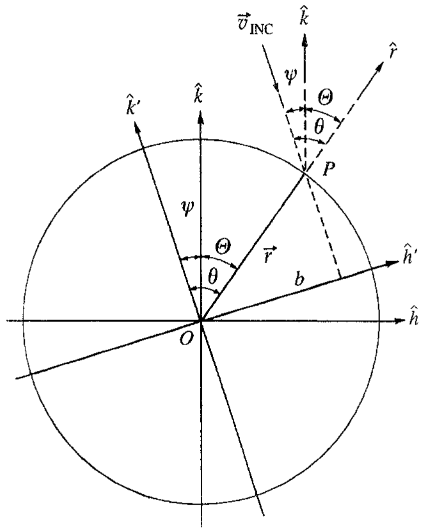

Figure 5. The collision problem involves the following information: I_1 and I_2 state that there is a molecule of diameter σ centered at O, and an identical molecule centered at the point P, of coordinates $|\vec{r}| = \sigma$, φ, and Θ; I_3 gives the direction of $\vec{v}_{\mathrm{INC}}$, which is Ψ; I_4 gives the magnitude of $\vec{v}_{\mathrm{INC}}$. A rotation of angle $\Psi = \theta - \Theta$ around the axis perpendicular to the plane of the figure through O brings $\hat{h}$ into $\hat{h}'$ and Θ into θ.

and I_2 also would be meaningless. In this sense, I_1 is part of the meaning of φ, b, and can not be separated from the part of I_2 that says the two molecules are colliding.

But if Condition A does not depend on I_3, the following reading of Proposition II is implied, as given in BURBURY's letter of November 22, 1894 (1894a):

> *For any given direction of* [*the relative velocity*] *R before collision,* all directions after collision are equally probable.[5]

4.4 Another consequence of the above considerations is that the independence of the distribution of φ, b (or θ) from I_3 (and I_4), as implied by Condition A, can be interpreted as a statistical independence between I_3, I_4, on the one hand, and φ, b, I_1, and I_2, on the other hand. Conversely, statistical independence between these two sets of information implies Condition A. For φ and b can be distributed on any great circle (the various great circles need not be equally probable, as shown below), but the remaining information, I_1 and I_2, although pertinent to fixing φ and b, is sufficiently meager to fix particular values for these variables; hence, there would be no information that would justify making one value for the impact parameter more likely than another. Thus, Condition A seems to express nothing more than the trivial fact

[5] My italics.

that when two molecules collide (I_2), the impact parameter is on *any* great circle of the collision sphere around the molecule at rest at the center of coordinates (I_1); Condition A expresses no more than a conjunction of I_1 and I_2. Perhaps this statistical independence is what BURBURY (1894b) meant when, on December 20, 1894, he added a cryptic remark to the assumption that the collision coordinates were "taken a[s] haphazard" (Condition A). His remark could be considered as a qualification of "haphazard"; according to it, the collision coordinates were to be taken "without regard to the variables $P'q'$ . . . ," which are the independent coordinates in phase space, not including the collision coordinates.

4.5 This result also has a geometrical interpretation. The mechanical problem shows that knowledge of φ and θ still leaves the (azimuthal) direction of the incoming velocity in absolute space completely undetermined. In fact, one can always rotate the plane containing the line joining the centers of the molecules and the incoming velocity around an axis through the center of the collision sphere, and perpendicular to the plane (Fig. 5). It is easy to prove that this rotation keeps invariant φ, θ, the area $b\,db\,d\varphi = \frac{\sigma^2}{4}\sin(2\theta)\,d(2\theta)\,d\varphi$ (and obviously I_2, since the center of the moving molecule is still on the collision sphere, and I_1, since the center of the target molecule is still at rest at the origin of coordinates), but changes the direction of the velocity of approach in absolute space and the direction of the line joining the centers of the molecules. That is, for the same φ, θ (and I_1, I_2), there are infinitely many directions of approach. The converse is also true: knowledge of the direction of approach gives no information about φ, θ (and, clearly, none about I_1 and I_2). From the mechanical point of view, there is thus an independence between two sets of variables: φ, θ (and the information I_1 and I_2, which give the meaning of φ and θ) and the azimuthal direction of the incoming relative velocity. Knowledge of the former leaves the latter undetermined, and perhaps this is why there is incomplete knowledge of the velocity, as our reading of BRYAN suggested. This might have been what BRYAN learned from BURBURY.[6]

[6] CLIFFORD A. TRUESDELL & R. G. MUNCASTER treated the problem of locating two molecules before and after a collision as a mapping problem. The result of my paper can be understood in the light of their analysis. I shall use the notation of the Appendix, of Figure 5, and of Figure 6. In doing so, the generality and elegance of their analysis is lost; however, there is a gain in the understanding of my analysis. Following BRYAN, let "unaccented" and "accented" quantities denote variables before and after collision, respectively, Let indices 1 and 2 denote the two molecules, respectively. Let $\mathscr{V}$ be the velocity space, and let $\mathscr{K}$ be a parameter space. According to TRUESDELL & MUNCASTER, a collision is a transformation Φ: $\mathscr{V}\times\mathscr{V}\times\mathscr{K}\to\mathscr{V}\times\mathscr{V}$, which associates to the triple $(\vec{v}_1, \vec{v}_2, \vec{\kappa})$ the pair $(\vec{v}'_1, \vec{v}'_2)$:

$$\Phi(\vec{v}_1, \vec{v}_2, \vec{\kappa}) = (\vec{v}'_1, \vec{v}'_2)\,.$$

4.6 Proposition II played a role in the theory. As was noted earlier, Proposition II was introduced by MAXWELL to show how collisions could randomize the direction of motion. In this regard, it is significant that when BRYAN invoked Condition A on December 20, 1894, he used the same example as CLAUSIUS had used some 30 years earlier to illustrate the "irregularity" of the molecular motion. And, like CLAUSIUS (1862), BRYAN too used the example to eliminate those "non-irregular" configurations, which were nevertheless allowed by mechanics. Thus, BURBURY probably knew, independently of the debate in *Nature*, that those collisions involved in the H-Theorem had to obey Proposition II, if they were to be the physical process causing equilibrium, and if the H-Theorem was to have any meaning at all. This consequence of Proposition II seems to be expressed in the following passage in BURBURY's letter of November 22 (1894a):

> Thus we have proved that if condition A be satisfied, then if *all directions of the relative velocity* for given V [the velocity of the center-of-mass] *are not now equally likely*, the effect of collisions is to make H diminish.[7]

In the notation of this paper, the transformation Φ is:

$$\vec{v}'_1 = \vec{v}_1 - |\vec{v}| \cos\theta\, \hat{r}$$

$$\vec{v}'_2 = \vec{v}_2 + |\vec{v}| \cos\theta\, \hat{r}\,.$$

The parameter space is the space of coordinates φ and θ.

Let $\mathscr{S}$ be a set lying in the plane perpendicular to the incoming relative velocity, $\vec{v}_{\text{INC}}$. $\mathscr{S}$ is such that if the impact parameter lies within $\mathscr{S}$ a collision occurs; in the notation of this paper, it is the great circle of the collision sphere perpendicular to $\vec{v}_{\text{INC}}$. TRUESDELL & MUNCASTER defined the Encounter Operator. This is a piecewise smooth mapping of $\mathscr{V} \times \mathscr{V} \times \mathscr{S}$ into itself:

$$E(\vec{v}_1, \vec{v}_2, b, \varphi) \equiv (\vec{v}_1 - |\vec{v}| \cos\theta\, \hat{r}, \vec{v}_2 + |\vec{v}| \cos\theta\, \hat{r}, b, \varphi)\,.$$

TRUESDELL & MUNCASTER showed how E varies by orthogonal transformations. Let Q be an orthogonal transformation over $\mathscr{V} \times \mathscr{V} \times \mathscr{S}$; let the same simbol also denote transformatioins over $\mathscr{V}$, and transformations over $\mathscr{S}$. Define Q as follows:

$$Q(\vec{v}_1, \vec{v}_2, \vec{\rho}) \equiv (Q\vec{v}_1, Q\vec{v}_2, Q\vec{\rho})\,;$$

$\vec{\rho} = \hat{r} \sin\theta, |\vec{\rho}| = b$, is the projection of the point of collision on $\mathscr{S}$ (E is viewed now as a function of $\vec{v}_1$, $\vec{v}_2$, and $\vec{\rho}$ rather than $\vec{v}_1, \vec{v}_2$, b, and φ). The Encounter Operator is invariant by orthogonal transformations over $\mathscr{V} \times \mathscr{V} \times \mathscr{S}$:

$$QE(\vec{v}_1, \vec{v}_2, \vec{\rho}) = E(Q\vec{v}_1, Q\vec{v}_2, Q\vec{\rho})\,.$$

Condition A is associated with the transformation that takes the cartesian coordinates x, y, and z, on $\mathscr{S}$, into the coordinates $\sigma \cos\varphi \sin(\Theta + \Psi)$, $\sigma \sin\varphi \sin(\Theta + \Psi)$, and $\sigma \cos(\Theta + \Psi)$, respectively. Equivalently, it takes $(\sigma, \varphi, \Theta)$ into $(\sigma, \varphi, \theta = \Theta + \Psi)$, where θ is the angle between $\hat{r}$ and $\vec{v}_{\text{INC}}$.

[7] My italics.

BURBURY expressed it more neatly in his letter of January 31, 1895:

> Then, as proved [Proposition II], *whatever the initial distribution* [of R], after collisions, the distribution of R is uniform, *i.e.*, all directions [are] equally probable.[8]

Actually, it is difficult to understand in this context what Proposition II proves. It is not the H-Theorem, but it does concern the approach to equilibrium, as MAXWELL and CLAUSIUS showed. Or, as BURBURY deceptively expressed it (1894b, p. 176): "I have assumed condition A. I do not say that is the only assumption that will answer the purpose. But it is sufficient." In any case, as already commented in Section 4.2, when challenged by CULVERWELL, BURBURY already knew where the possibility of reversal could fail, since his answer was prompt.[9] But if Condition A can be expressed as a sufficient condition for Proposition II to perform its role, this is because it is not incompatible with the mechanics of collision expressing allowed symmetries, which concern the independent degrees of freedom.

4.7 At this point it might be tempting to conclude that the distribution of the direction of the relative velocity is isotropic around the molecule at the center of the collision sphere, since there seems to be no information justifying one direction over another. This need not be the case. It suffices for BURBURY's argument that Condition A be true both in equilibrium and in non-equilibrium, while the particular distribution of velocities existing at a certain instant may describe a state of a gas away from equilibrium. For, if Condition A holds, there is a piece of information which is correlated to one set of variables, but is statistically independent of the other. Indeed, this seems to be the correct assumption to make, since BURBURY did not preclude that Condition A be true in equilibrium. On the contrary, equilibrium means that Condition A is true for both the direct and the reversed motions (1895a):

> If condition A is fulfilled in the reversed motion, then after reversed collisions the distribution of R is uniform. It is equally certain that it must be the same as the initial distribution.
>
> If, therefore, condition A is fulfilled in the reverse motion as well as in the direct, that can only be because the distribution of R was uniform to begin with. But that means that H was minimum to begin with, and therefore $\frac{dH}{dt} = 0$ throughout.

It should be emphasized that Condition A fails in the reversed motion, because the "collision coordinates" become known, as observed by BRYAN, not because Condition A ceases to be true in equilibrium, or when the velocity is randomized.

---

[8] My italics.

[9] CULVERWELL's first letter was published on October 25, 1894, and BURBURY's answer was dated November 12; therefore there were only 18 days between them.

4.8 In my reading, then, Proposition II was fundamental to the interpretation and recognition of the *Stosszahlansatz* in the 1894–1895 debate in *Nature*. Condition A expresses symmetries of the mechanical problem of a collision between two spheres; these symmetries arise from the indefinitness of the "collision coordinates".

BURBURY's priority in identifying the *Stosszahlansatz* as *the* statistical hypothesis in the proof of the H-Theorem was recognized by BOLTZMANN a few years later (1896, p. 40):

> In this formula [the *Stosszahlansatz*] there is contained a special assumption, as Burbury has clearly emphasized.

Significantly, BOLTZMANN cited BURBURY's first letter to *Nature*, dated November 22, 1894. BOLTZMANN himself would introduce the *Stosszahlansatz* with arguments that were reminiscent of Condition A and Proposition II.

BOLTZMANN's intervention in the debate consisted of two letters to *Nature*, published, respectively, on February 28, 1895 (1895a) and July 4, 1895 (1895b). In the first letter, he explained the statistical nature of his theorem; here he used the famous analogy of the "inverted tree." It was after this letter that the debaters started to come into agreement, although BOLTZMANN did not state what his statistical hypothesis was. The second letter is more interesting for my purposes. In it BOLTZMANN justified the *Stosszahlansatz* with the following argument: If the mean free path is long compared to the mean distance between two neighboring molecules, then two successive collisions of the same molecule occur at places that are far away from each other; consequently (1895b):

> [T]he distribution of the molecules surrounding the place of the second impact will be independent of the conditions in the neighbourhood of the place where the first impact occurred, and therefore independent of the motion of the molecule itself.

According to BOLTZMANN, a necessary condition for the *Stosszahlansatz* to hold is that the molecules *be not* (1895b) "arranged intentionally in a particular manner," as they were in BRYAN's example (Section 3.4). The same argument would be repeated in BOLTZMANN's book (1896) years later; from it BOLTZMANN concluded, analogously to his intervention in the debate in *Nature* (1896, p. 41):

> [I]f we chose the initial configuration on the basis of the path of each molecule, so as to violate intentionally the laws of probability, then of course we can construct a persistent regularity . . . .

BURBURY, in a paper of 1904, seems to have adopted BOLTZMANN's picture of the *Stosszahlansatz*, perhaps as a short-cut for his more detailed picture based on Proposition II (1904, p. 46):

> That statement [the *Stosszahlansatz*] involves a physical assumption of the most important and far-reaching character, namely . . . that the chance of a molecule having velocities within the assigned limits is at every instant independent of the positions and velocities of all the other molecules for the time being. For if not, the number of collisions between m and m' is not necessarily proportional to the product of $f\, du_1 \ldots dw_n$ and $f'\, du'_1 \ldots dw'_n$, because there may exist a stream by virtue of which m and m' have on average velocities of the same sign, and that affects the frequency of such collisions. It may conceivably be true that there are no such streams, but it is not axiomatic.

4.9 Finally, a side comment. We saw that, since his very first letter to *Nature*, BURBURY knew that the incoming velocity could have any distribution around the molecule at the center of the collision sphere. BRYAN said that he meant in his letter of December 20, 1894, that the two molecules had statistically independent velocities, and that he learned this from BURBURY; furthermore, in his 1894 Report, BRYAN correctly recognized the *Stosszahlansatz* and, again, gave credit to BURBURY. But both BURBURY and BRYAN missed obvious opportunities between November 22 and December 20 to recognize the *Stosszahlansatz* and to associate it with Condition A in their letters. I suspect that the debaters did not understand each other, initially, and did not agree as to what was being discussed. BURBURY seemed much more concerned to explain that there was a hypothesis that failed in the reversed motion, while BRYAN seemed more concerned to explain why it failed, and neither seemed concerned to interpret and analyze the hypothesis. And most probably, BRYAN was motivated by BURBURY's first letter (and, for that matter, his second as well), which left unexplained why Condition A was not true in the reversed motion. As BURBURY himself conceded (1895a):

> I said in my first letter on this subject that the condition A, on which, or its equivalent, the proof is based, could not apply to the reversed motion. As that assertion has been questioned, may I confirm it thus?

The story did not end here, however. What followed has been widely discussed in the literature. It suffices to say that BURBURY recognized another difficulty in the H-Theorem. If collisions bring about statistical correlations, then, he asked (1895b, p. 104–105) "does it necessarily follow that condition A, being now satisfied, will continue to be satisfied for all time?"

The EHRENFESTS recognized two different hypotheses, the "*Stosszahlansatz*" and the hypothesis of "molecular chaos," which says that the *Stosszahlansatz* holds "almost always." When, therefore, CULVERWELL asked his question, he addressed enduring issues pertaining to the conceptual foundation of the theory of heat. Rigorous and satisfactory solutions to these issues are far from having been achieved and are still open to research.

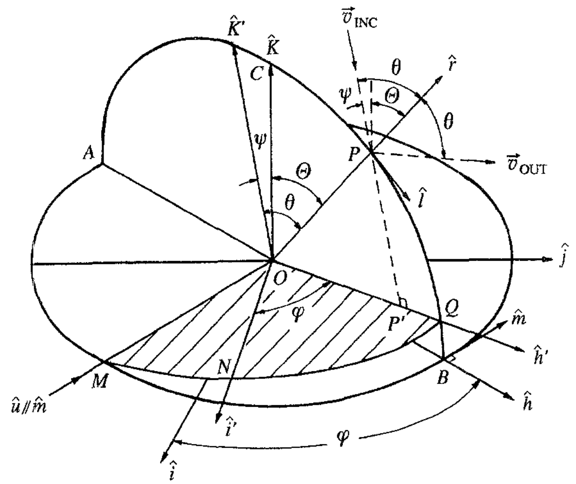

Figure 6. There is a group of rotations that leaves invariant φ (the plane of collision) and θ (the angle between $\hat{r}$ and $\vec{v}_{\mathrm{INC}}$), but not the direction of $\vec{v}_{\mathrm{INC}}$: These are the rotations of an angle $\Psi = \theta - \Theta$ (Θ variable) of the collision plane, around the axis $\vec{u}$, perpendicular to the plane. In particular, the "vertical", $\vec{k}$, can be brought into a new "vertical", $\vec{k}'$, parallel to $\vec{v}_{\mathrm{INC}}$.

5. Appendix: The Geometry of Proposition II

The collision problem is well known (C. CERCIGNANI, OSCAR E. LANFORD III, STEWART HARRIS). In particular, CLIFFORD A. TRUESDELL & R. G. MUNCASTER have analysed in great detail the symmetries of collisions.[10]

The geometry of the collision problem is illustrated in Figures 5 and 6. The circles are great circles of the collision sphere, of radius σ. The vector $\overrightarrow{\mathrm{OP}} \equiv \vec{r}$ joins the centers of the molecules at collision; $\vec{v}_{\mathrm{INC}}$ and $\vec{v}_{\mathrm{OUT}}$ are, respectively, the

[10] TRUESDELL & MUNCASTER gave a rigorous development to MAXWELL's kinetic theory. They tried to get as far as possible without the BOLTZMANN equation, in order to understand where it enters. They introduced the Collision Operator (p. 91) "as an axiom on which to base the mathematical theory." Using the notation of this paper, the Collision Operator, C, is given by $CF = \int_{\mathscr{V}} \int_{\mathscr{S}} v(F_1'F_2' - F_1F_2)\, dS\, d\vec{v}_2$. They show that this operator is invariant by orthogonal transformations. They also define the operator $\bar{C}_F g = \int gCF$, for any function $g(t, \vec{r}, \vec{v})$ that renders the integrals convergent. Then they prove (their equation (VII.21)) that $\bar{C}_F$ cannot be negative. With this as background, they discuss BOLTZMANN's theorem. Only in a later chapter do they introduce BOLTZMANN's equation. In this way, TRUESDELL & MUNCASTER show that the collision operator does something specific and precise and undergirds the BOLTZMANN's equation.

incoming and outgoing relative velocities. The solution of the collision problem is as follows:

(1) Conservation of linear momentum implies that the velocity of the center-of-mass is left invariant by the collision. Hence the only forces acting during collision are internal forces obeying NEWTON's third law, and the center-of-mass and the internal motion behave independently.
(2) Conservation of energy implies conservation of the magnitude of the relative velocity: $|\vec{v}_{\mathrm{INC}}| = |\vec{v}_{\mathrm{OUT}}| = |\vec{v}|$.
(3) The constraint that $\vec{v}_{\mathrm{INC}}$ and $\vec{r}$ intersect at P means that there exists a great circle, defined by φ, containing both $\vec{r}$ and $\vec{v}_{\mathrm{INC}}$ (great circle ACB in Figure 6). Now, conservation of angular momentum implies that $\vec{v}_{\mathrm{OUT}}$ also belongs to this great circle and that its angle with $\vec{r}$ is the same as the angle between $\vec{r}$ and $\vec{v}_{\mathrm{INC}}$. Consequently, the "collision coordinate" φ fixes the plane containing $\vec{v}_{\mathrm{INC}}$, $\vec{v}_{\mathrm{OUT}}$, and $\vec{r}$; and θ gives, on this plane, the directions of both $\vec{v}_{\mathrm{INC}}$ and $\vec{v}_{\mathrm{OUT}}$ with respect to $\vec{r}$:

$$\vec{v}_{\mathrm{INC}} = -|\vec{v}|\cos\theta\,\hat{r} \pm |\vec{v}|\sin\theta\,\hat{l}; \quad \vec{v}_{\mathrm{OUT}} = +|\vec{v}|\cos\theta\,\hat{r} \pm |\vec{v}|\sin\theta\,\hat{l}.$$

It is always possible to rotate the axes by an angle Ψ around an axis $\hat{u}$ through the origin, perpendicular to the circle ACB, hence parallel to the direction $\hat{m}$. This is the rotation that takes x into $\sigma\cos\varphi\sin(\Theta+\Psi)$, y into $\sigma\sin\varphi\sin(\Theta+\Psi)$, and z into $\sigma\cos(\Theta+\Psi)$; it leaves φ invariant, as well as θ, since its result is only to add a constant quantity, Ψ, to the azimuth, Θ. By conveniently choosing Ψ, it is possible to bring $\hat{k}$ into $\hat{k}'$, parallel to $\vec{v}_{\mathrm{INC}}$, as in Figures 5 and 6. Let, then, the shadowed great circle, MNQ, be the new "horizontal" plane. The impact parameter is, by definition, $b = OP'$. Trivially, any area $dx'\,dy'$ on MNP is left invariant: $dx'\,dy' = b\,db\,d\varphi = \sigma^2 \cos\theta\sin\theta\,d\theta\,d\varphi$, which is independent of Ψ or of the direction $\hat{k}'$ of MNP in absolute space. This rotation also keeps the components of $\vec{v}_{\mathrm{INC}}$ and $\vec{v}_{\mathrm{OUT}}$ along $\hat{r}$ and $\hat{l}$ (and in this limited sense this rotation represents a symmetry), but of course it changes the absolute components of $\hat{r}$ and $\hat{l}$ or, if one prefers, the point of impact P.

If now Condition A is a reasonable probability assignment, then it has a geometrical counterpart, because there is a group of rotations which leaves θ and φ invariant, but not Ψ. However, for fixed Ψ, it is always possible to change φ and θ. A change of φ corresponds to a rotation of axes $\hat{\imath}', \hat{\jmath}'$ (or of ACB) around $\hat{k}'$; the change of θ corresponds to a rotation of $\hat{r}$ alone (not of ACB as a whole) around $\hat{u}$. Thus Condition A seems to be reasonable.

Acknowledgements. I thank Professor ROGER H. STUEWER for the special attention given to my paper; his efforts to provide careful refereeing go beyond editor's duty. I am grateful to Professor CLAYTON GEARHART for reading and commenting on various versions of this paper; his suggestions certainly enriched the paper and clarified the argument. My gratitude to Professor ABNER SHIMONY is endless; I am indebted to him not only for his comments on this particular paper, but also for his continuous guidance and support.

References

BOLTZMANN, L. (1872) "Further Studies on the Thermal Equilibrium of Gas Molecules," translated in S. G. BRUSH (1965, 1966, 1972), vol. 2, pp. 88–175.

BOLTZMANN, L. (1877) "On the relation of a General Mechanical Theorem on the Second Law of Thermodynamics," translated in S. G. BRUSH (1965, 1966, 1972), vol. 2, pp. 188–202.

BOLTZMANN, L. (1895a) "On certain questions of the Theory of Gases," *Nature*, **51**, p. 413.

BOLTZMANN, L. (1895b) "On the Minimum Theorem in the Theory of Gases," *Nature*, **52**, p. 221.

BOLTZMANN, L. (1896) *Lectures on Gas Theory*, translated by S. G. BRUSH, University of California Press, Berkeley and Los Angeles, 1964.

BRUSH, S. G. (ed) (1965, 1966, 1972) *Kinetic Theory*, 3 vols, Pergamon Press, Oxford.

BRUSH, S. G. (1976) *The Kind of Motion We Call Heat*, 2 vols., North-Holland, Amsterdam.

BRYAN, G. H. (1891) "Researches Related to the connection of the Second Law with Dynamical Principles," *British Association Report*, **61**, pp. 85–122.

BRYAN, G. H. (1894a) "Report on the Present State of our Knowledge of Thermodynamics," *British Association Report*, **64**, pp. 64–106.

BRYAN, G. H. (1894b) "The Kinetic Theory of Gases," *Nature*, **51**, p. 176.

BRYAN, G. H. (1895) "The Assumption in Boltzmann's Minimum Theorem," *Nature*, **52**, pp. 29–30.

BURBURY, S. H. (1886) "The Foundations of the Kinetic Theory of Gases," *Philosophical Magazine*, [5], **21**, pp. 481–483.

BURBURY, S. H. (1890) "On some Problems in the Kinetic Theory of Gases," *Philosophical Magazine*, [5], **30**, pp. 298–317.

BURBURY, S. H. (1891) "On the Collision of Elastic Bodies," Abstract, *Proceedings of the Royal Society of London*, **50**, pp. 175–179.

BURBURY, S. H. (1892) "On the Collision of Elastic Bodies," *Philosophical Transactions*, **183 A**, pp. 407–422.

BURBURY, S. H. (1894a) "Boltzmann's Minimum Function," *Nature*, **51**, p. 78–79.

BURBURY, S. H. (1894b) "The Kinetic Theory of Gases," *Nature*, **51**, pp. 175–176.

BURBURY, S. H. (1895a) "Boltzmann's Miminum Function," *Nature*, **51**, p. 320.

BURBURY, S. H. (1895b) "Boltzmann's Minimum Function," *Nature*, **52**, pp. 104–105.

BURBURY, S. H. (1904) "On the Theory of Diminishing Entropy," *Philosophical Magazine*, [6], **8**, pp. 43–49.

CERCIGNANI, C. (1972) "On the Boltzmann Equation for Rigid Spheres," *Transport Theory and Statistical Physics*, **2**, p. 211–225.

CLAUSIUS, R. E. J. (1858) "On the mean lengths of the paths described by the separate molecules of gaseous bodies," translated by F. GUTHRIE (1859), republished in S. G. BRUSH (1965, 1966, 1972), vol. 1, pp. 135–147.

CLAUSIUS, R. E. J. (1862) "On the conduction of Heat by Gases," translated by G. C. FOSTER (1862) in *Philosophical Magazine*, [4], **23**, pp. 417–435, 512–534.

CULVERWELL, E. P. (1894a) "Dr. Watson's Proof of Boltzmann's Theorem on Permanence of Distributions," *Nature*, **50**, p. 617.

CULVERWELL, E. P. (1894b) "Boltzmann's Minimum Theorem," *Nature*, **51**, p. 105.

CULVERWELL, E. P. (1895a) "Boltzmann's Minimum Theorem," *Nature*, **51**, p. 246.

CULVERWELL, E. P. (1895b) "Professor Boltzmann's letter on the kinetic theory of Gases," *Nature*, **51**, p. 581.

EHRENFEST, P. and T. (1911) *The Conceptual Foundations of Statistical Mechanics*, translated by M. J. MORAVCSIK, Cornell University Press, republished by Dover, New York, 1958.

GRAD, H. (1958) "Principles of the Kinetic Theory of Gases," in S. FLÜGGE (ed.), *Thermodynamics of Gases*, Encyclopaedia of Physics, vol. XII, Springer-Verlag, Berlin, pp. 205–294.

HARRIS, STEWART (1971) *An Introduction to the Theory of the Boltzmann Equation*, Holt, Rinehart and Winston, New York.

KLEIN, M. J. (1973) "The Development of Boltzmnann's Statistical Ideas," in E. G. D. COHEN & W. THIRRING (eds) *The Boltzmann Equation: Theory and Applications*, Springer-Verlag, Berlin, pp. 53–105.

KUHN, T. S. (1978) *Black-body Theory and the Quantum Discontinuity 1894–1912*, Oxford.

LANFORD III, O. E. (1975) "Time Evolution of Large Classical Systems," in J. MOSER (ed.) *Dynamical Systems, Theory and Applications*, Lecture Notes in Physics, **38**, Springer-Verlag, Berlin, pp. 1–111.

MAXWELL, J. C. (1860) "Illustrations of the Dynamical Theory of Gases," *Philosophical Magazine*, [4], **19**, pp. 19–32, **20**, pp. 21–37. Republished in W. D. NIVEN (ed.) (1890), vol. 1, pp. 377–409. Also republished in part in S. G. BRUSH (ed) (1965, 1966, 1972), vol. 1, pp. 148–178.

MAXWELL, J. C. (1866) "On the Dynamical Theory of Gases," *Philosophical Transactions of the Royal Society of London*, **157**, pp. 49–88. Reprinted in W. D. NIVEN (ed.) (1890), vol. 2, pp. 26–78. Also reprinted in S. G. BRUSH (ed.) (1965, 1966, 1972), vol. 2. pp. 23–87.

NIVEN, W. D. (1890) *The Scientific Papers of James Clerk Maxwell*, 2 vols, Cambridge University Press; republished by Dover, New York, 1961.

TRUESDELL, C. A. & MUNCASTER, R. G. (1979) *Fundamentals of Maxwell's Kinetic Theory of a Simple Monatomic Gas* (*Treated as a Branch of Rational Mechanics*), Academic Press, New York.

WATSON, H. W. (1876) *A Treatise on the Kinetic Theory of Gases*, First Edition, Clarendon, Oxford.

WATSON, H. W. (1893) *A Treatise on the Kinetic Theory of Gases*, Second Edition, Clarendon, Oxford.

WATSON, H. W. (1894) "Boltzmann's Minimum Theorem," *Nature*, **51**, p. 105.

Instituto de Física
Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil

and

Centro de Lógica, Epistemologia & História da Ciência
Universidade Estadual de Campinas
Campinas, Brazil

(Received July 5, 1993)