The H-Theorem, Molecular Disorder and Probability: Perspectives from Boltzmann's Lectures on Gas Theory

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Abstract

This paper examines Boltzmann's responses to the Loschmidt reversibility objection to the H-theorem, as presented in his Lectures on Gas Theory. I describe and evaluate two distinct conceptions of the assumption of molecular disorder found in this work, and contrast these notions with the Stosszahlansatz, as well as with the predominant contemporary conception of molecular disorder. Both these conceptions are assessed with respect to the reversibility objection. Finally, I interpret Boltzmann as claiming that a state of molecular disorder serves as a necessary condition for the application of probabilistic arguments. This in turn offers a way to bridge the conceptual gap between the H-theorem and his combinatorial argument.

1. Introduction

Foundational discussions of Boltzmann's H-theorem have a long and chequered history. Among the central problems facing both historical and foundational scholarship concerning Boltzmann's work are the proper interpretation of the Stosszahlansatz, its later incarnation as the Assumption of Molecular Chaos, his understanding of probability and its application to physical theory, and how the H-theorem is related to the combinatorial argument he presented as a reply to Loschmidt's objection. Although these issues have been much discussed, this paper endeavours to cast new light on how Boltzmann came to see these matters in his later work, the Lectures on Gas Theory (LGT) published in two volumes in 1896 and 1898. As this paper will attempt to demonstrate, a very different picture of Boltzmann's thought emerges in these writings, one that is significantly different from the perspectives he offered in his initial treatments of these issues and also from the received view passed down through the literature. Specifically, this paper looks to defend the following theses:

1. Boltzmann's notion of molecular disorder in the LGT differs from both the Stosszahlansatz and the various notions of molecular disorder found in

the foundational and physics literature. Two such notions of molecular disorder will be introduced and discussed.

2. Although no clear interpretation of probability will be proposed, Boltzmann saw the condition of molecular disorder as a necessary precondition for the application of the probability calculus to the description of statistical mechanical systems.
3. Boltzmann saw the condition of molecular disorder as a bridge between the H-theorem and the combinatorial argument, thus explaining how the combinatorial argument rebuts Loschmidt's objection.

Although these topics are intimately wrapped up with Boltzmann's explication of irreversibility and time-asymmetry, these issues will largely be passed over in this paper, and left to further work.

Boltzmann, in 1872, proved his H-theorem that demonstrated that no matter how the velocities of the molecules in a gaseous system are initially distributed, the velocity distribution would evolve via successive collisions to the stationary, Maxwellian distribution. The proof claimed to be completely general, but Loschmidt (1876) identified an apparent counterexample to the theorem: if one took a system that had evolved from a non-stationary state to the stationary one and reversed the direction of the velocity of each molecule, then the deterministic laws of motion would guarantee that the system would retrace its evolutionary path back to the non-stationary state.

Boltzmann's (1877b) most thorough response to Loschmidt eschewed dynamical considerations altogether, and offered a combinatorial argument claiming that among the particular distributions of velocities and positions of the molecules (complexions), the Maxwellian velocity distribution could be realised in the greatest number of ways, and the complexions of any other distribution were relatively few in number and hence very improbable. Thus, a system initially in an improbable state would most likely evolve to the most probable one, and remain there indefinitely.

These moves evade the gist of Loschmidt's objection, as Loschmidt intended his reversibility argument as an objection to the validity of the H-theorem. Yet Boltzmann appears to skirt the central issue by changing the terms of the debate. What might be called a received interpretation of this move is that Boltzmann completely reconceived the role played by and interpretation of probability in kinetic theory, and also came to realise the statistical nature of the 2nd law of thermodynamics in response to Loschmidt (Klein 1973). As such, Boltzmann supposedly abandoned the derivation of the H-theorem as a universally valid theorem in favour of the combinatorial argument, replacing considerations based on the collisions of molecules with an abstract ‘counting’ argument.

If this is true, Boltzmann’s change of heart did not last, for in the LGT, the character of his response to Loschmidt takes on a very different form. Indeed, discussions of the reversibility argument are almost always linked back to the deduction of the H-theorem (e.g. 1896, 58-59 and 1898, 441-444), though he retains the combinatorial argument as well. Boltzmann points out that the quantity H has a “twofold” meaning, one mathematical and one physical. Boltzmann does not intend these two interpretations of H to be exclusive, but rather complementary. Insofar as Boltzmann’s initial combinatorial reply to Loschmidt appears to be a purely ‘mathematical’ argument, one might well wonder how this argument addresses Loschmidt’s ‘physical’ objection’; that is, one based on dynamical and collisional considerations.

Although Boltzmann’s detailed responses to Loschmidt are not the focus of this paper, it is widely recognised that Boltzmann’s views on the nature of time, entropy and probability were deeply affected by the reversibility objection. Here, I would like to suggest a different reading of Boltzmann’s views on these issues from the perspective of his most exhaustive mature work, the LGT. In section 2 of the paper, I briefly review Boltzmann’s H-theorem and the combinatorial argument. The next section discusses and explores some distinctions between the related notions of molecular disorder (or molecular chaos) and the Stosszahlansatz that was the key assumption in the derivation of the H-theorem. These notions are less than clear and not always distinct in Boltzmann’s own writings, and this section will attempt to clarify and analyse some different ways in which these notions are employed in the contemporary literature. Section 4 will introduce two possible readings of Boltzmann’s understanding of molecular disorder, comparing and contrasting them to the conceptions discussed in section 3. The final substantive section of the paper investigates how Boltzmann proposes to link the ‘mathematical’ and ‘physical’ meanings of H by restricting the application of the combinatorial argument (and probabilistic arguments more generally) to systems that are molecular disordered; that is, to systems where the H-theorem holds.

2. The H-Theorem and the Combinatorial Response to Loschmidt

2.1 The H-Theorem

Boltzmann (1872) attempts to demonstrate how, on the basis of purely mechanical considerations, a gas away from equilibrium approaches its unique, stationary state characterised by the Maxwellian distribution. In order to do so, he defines the velocity distribution *f* of the components of a gas, and further assumes that the directions of the velocities are all equally probable and that the gas is spatially uniform with respect to the velocity distribution. If, for a given collision between two molecules with energies between $x+dx$ and $x'+dx'$ before the collision, and energies between $y+dy$ and $y'+dy'$ after the collision, respectively, the number of collisions in a time τ can be written as

$$dn = \tau f(x,t)dxf(x',t)dx'\,dy\varphi(x,x',y)$$

where the function $\varphi(x,x',y)$ is determined by the specific kinds of collisions appropriate for the system. The variable y' drops out of the equation since the system is constrained by the conservation of energy, i.e. $x+x'=y+y'$. Here the key assumption is that the velocity distributions for the two particles are uncorrelated, and hence the total distribution of velocities for the pair of particles can be written as the product of two independent distributions. This assumption is the famous Stosszahlansatz (SZA), which was later identified as the key to the proof. After some manipulations, Boltzmann deduces that the change in the distribution function is given by

$$\frac{\partial f(x,t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(y,t)}{\sqrt{y}}\frac{f(x+x'-y,t)}{\sqrt{x+x'-y}} - \frac{f(x,t)}{\sqrt{x}}\frac{f(x',t)}{\sqrt{x'}}\right]\sqrt{xx'}r(x,x',y)dx'\,dy$$

and demonstrates that the Maxwellian distribution is a stationary state, in the sense that the above equation is equal to zero for that distribution. Boltzmann also postulates the quantity H as an analogue (up to a constant multiplicative factor) for the thermodynamic entropy

$$H = \int_0^\infty f(x,t)\left[\log\left(\frac{f(x,t)}{\sqrt{x}}\right) - 1\right]dx$$

and demonstrates that this quantity, as the result of the collisions, always decreases over time except when it reaches the stationary state, at which point it remains constant.

Hence, through molecular collisions, Boltzmann claims to show that any system with an arbitrary initial velocity distribution will monotonically increase in entropy until it reaches the Maxwellian, equilibrium distribution.

2.2 The Combinatorial Argument

In his 1877 responses to Loschmidt, the mechanical derivation of the H-theorem gives way to a combinatorial analysis that is intended to demonstrate, on the basis of purely probabilistic considerations, that any state that is not the stationary, equilibrium state will quickly evolve to that state, seemingly independent of any dynamical properties of the system. Boltzmann (1877b) considers a 6-dimensional μ-space, where the dimensions represent the three spatial and momentum coordinates of a particle.[1] This space is partitioned into many small and disjoint (6-dimensional) rectangular cells, and is filled with points representing the N particles that comprise the gas, where each possible distribution is called a complexion. The macrostate of the gas can then be described as the number of particles that occupy each of these rectangular regions of the μ-space. The relative probability of each macrostate Γ is then given by a combinatorial analysis expressed by

$$|\Gamma| \propto \frac{N!}{n_1!n_2!\ldots n_m!}$$

where the n_i are the number of particles in the *ith* cell of the μ-space. If there are many molecules in each cell, the Stirling approximation gives the result

$$\log|\Gamma| \approx N\log N - \sum_i n_i \log n_i$$

which Boltzmann identifies as corresponding to the entropy, and whose negative value is equal to the quantity H identified in 1872 if the gas molecules are uniformly distributed in space. Through the technique of Lagrange multipliers, constrained by the total particle number N and the total energy of the system, one recovers the spatially uniform Maxwell velocity distribution as by far the most probable macrostate.

3. The Stosszahlansatz and the Assumption of Molecular Chaos

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[1] It is worth noting that this combinatorial argument includes consideration of the positions of the molecules, whereas the H-theorem only describes the velocity distribution.

Perhaps one of the greatest impediments to understanding Boltzmann's work is developing a clear understanding of his response to Loschmidt's reversibility objection. Historically, the story follows a strange path: after proving the H-theorem, apparently demonstrating the monotonic decrease in the value of the H-function to be a clear consequence of the laws of mechanics, Loschmidt offered what appeared to be a damning objection to the argument: he claimed that there were, given the mechanical picture under which Boltzmann was working, circumstances where H would increase. Boltzmann appears to have accepted Loschmidt's argument as obvious, but at the same time calls it a "fallacy" and a "sophism" (1877a). Instead of addressing Loschmidt's criticism from a mechanical perspective, Boltzmann (1877b) then offers a combinatorial argument to the effect the states that Loschmidt considers are extremely rare and improbable, and that it is clear that the H-theorem only holds with high probability. Boltzmann's responses in 1877 suggest a break from his previous thought in at least two important ways:

1. The notion of probability he uses shifts from its identification with the velocity distribution of a system to a measure over the possible states of the system consistent with its total energy. (Klein 1973)
2. The combinatorial argument eschews any mechanical considerations and shifts to one that argues that any state other than the most probable (equilibrium) one is highly unlikely, in contradistinction to the H-theorem that focuses on particle collisions.

Between Boltzmann's 1877 replies to Loschmidt and the LGT, Burbury, Bryan and others first identified the culprit in the derivation of the H-theorem that was responsible for the time-asymmetric, irreversible behaviour: the SZA that claimed that colliding molecules velocities were uncorrelated before the collision but became correlated afterwards.[2] Clearly it is this assumption that is violated in Loschmidt's scenario: the reversal of the velocities of each particle would apparently lead to an evolution where the molecules began as correlated before the collisions, and then became uncorrelated afterwards.

When viewed in this light, Loschmidt's argument cannot be answered by a purely 'mathematical' or combinatorial interpretation of the H-theorem, but requires a 'physical' response. Ideally, such a response, if it is to make contact with the arguments that Boltzmann made almost twenty years earlier, should justify (in some sense) the use of

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[2] See Brush (1976, 616-627) for a detailed review of the notion of molecular disorder and the debate over the Stosszahlansatz. Also see Kuhn (1978).

combinatorial methods and the conception of probability associated with it. We begin by examining Boltzmann's SZA, its reinterpretation at the Assumption of Molecular Chaos (AMC) in contemporary literature, with an eye to contrasting these notions with the conception of molecular disorder that Boltzmann presents.

A standard reading of Boltzmann's SZA is that it cannot be understood either as a direct consequence of the laws of mechanics or of the theory of probability. Against the first claim, one need only note that the SZA is a time-asymmetric notion, whereas the laws of mechanics are time-symmetric. Against the second point, the SZA is a claim about correlations between the velocities of mechanical particles, and surely the laws of probability themselves say nothing about physical properties. So what is the Stosszahlansatz? The most common interpretation is that the assumption is one about the state of the gas, a state such that as the gas evolves, the velocities of colliding molecules are uncorrelated *before* they collide but are correlated *afterwards* (Uffink 2006). But in the LGT, Boltzmann replaces the SZA with the AMC, or the assumption that the system is molecular-disordered.

I shall understand the SZA to be an explicitly time asymmetric assumption, one that claims that the velocity distribution of colliding molecules are uncorrelated *before* they collide, but makes no claim as to their state of correlation following their collisions. Intuitively, this silence regarding their post-collision state is obvious: colliding molecules are likely to be correlated given their interaction. If this assumption holds at all times, its time-asymmetric nature underwrites the time-asymmetric conclusion of the H-theorem.

Conversely, the AMC is a claim about the instantaneous state of the system; it usually is formulated as the assertion that there exist no correlations between the velocities of all pairs of molecules (e.g. Huang 1963). At first glance, this is apparently a much stronger condition than the SZA, for two reasons:

1. The SZA is time asymmetric. It refers only to the existence of correlations in one temporal direction only. Conversely, the AMC makes a general claim about the existence of correlations between pairs of molecules without specifying a temporal orientation.
2. The SZA is limited to a claim about colliding molecules in that it refers only to correlations between molecules about to collide. By contrast, the AMC is much more liberal in that it refers to *all pairs* of molecules, not just those about to collide. Included in this latter condition are molecules that have already collided, and molecules that do not collide at all (at least on the relevant time scales).

Given the strength of the AMC relative to the SZA, it is tempting to conclude that it is a strictly stronger condition than the SZA; that is, the AMC implies the SZA. But as Brown and Myrvold (2008) note, this is not so: it is perfectly possible that a subset of all pairs of molecules exhibit correlations even though the set of all pairs does not, and it is certainly a logical possibility that the subset comprising the pairs of molecules about to collide is among such subsets. Further, the SZA requires the specification of a temporal interval τ to calculate the number of collisions in a chosen time interval, whereas the AMC does not need any such specification. Thus, the AMC represents a much more demanding condition, but one that is logically independent of the SZA.

There is something of a puzzle here. On the one hand, the SZA is objectionable because it is an explicitly time-asymmetric assumption, and one does not want to sneak in the time-asymmetric behaviour predicted by the H-theorem without a proper justification. On the other hand, the putative advantage of the AMC, namely its time symmetric nature, comes at the cost of its being a far stronger condition and moreover, one that does not even guarantee the independence of incoming colliding molecules upon which the validity of the H-theorem depends. Indeed, a naïve application of the AMC implies that the H-theorem holds in both temporal directions, in the sense that if the AMC sufficed as the independence condition required for the H-theorem, it would imply that the H-theorem would only be valid for local peaks in the H-curve due to the time symmetric dynamics (Huang 1963), and could not demonstrate the globally decreasing trend in the H-curve that is the desired result of the H-theorem.

Nonetheless, the problem for the AMC, in that it does not immediately provide the condition required for the H-theorem to hold, is easy to identify: it is not sufficiently sensitive to the crucial feature that distinguishes it from the SZA; that is, it is not focused on colliding molecules, or at least the localised correlations that are necessary for treating the interactions between molecules. Indeed, it is this very issue that arises in Brown and Myrvold's critique of Eggarter (1973). Eggarter uses a somewhat idiosyncratic definition of the SZA, one that establishes it as a strictly weaker claim than the AMC: he defines the SZA as the condition that the system behaves *as if* the AMC were true. Naturally, the AMC is then sufficient for this notion of the SZA, and Eggarter constructs a model to show that it is not necessary. As such, Eggarter's claim is true by definition, but the presupposition behind his analysis is that the SZA does in fact serve as sufficient assumption for the proof of the H-theorem. What Brown and Myrvold show is that this notion of the SZA, and indeed the full AMC, cannot serve the role that is required to generate a monotonic decrease in the H-curve.[3]

4. The Molecular Disorder Condition

However, the AMC discussed thus far is not Boltzmann's. In what follows I will present and preliminarily evaluate two possible understandings of Boltzmann's conception of molecular disorder. Boltzmann's notions of molecular disorder, like the SZA, refer only to local correlations, though they do not specifically restrict themselves to molecules that do in fact collide, but instead focus on nearby molecules whether they collide or not. As a consequence, these conditions are not necessarily about individual *pairs* of molecules, but groups of molecules near one another irrespective of whether they previously collided, will collide or do not collide at all. As a result, these conditions can become difficult to specify in a formal way, but demonstrate Boltzmann's sensitivity to the issues discussed above.

4.1 One notion of Molecular Disorder

Boltzmann (1896, 37-40) considers the frequency of collisions between two types of molecules, labelled m and m_1, with velocities in the ranges $d\omega$ and $d\omega_1$, respectively (where f and F denote the velocity distribution functions per unit volume of the two kinds of molecules respectively).[4] He then constructs a unit sphere at the coordinate origin, and defines a surface element on this sphere $d\lambda$ such that a line connecting the two molecules is parallel to a radial line element from the origin to the surface $d\lambda$, defining a cone. The relative velocity of m relative to m_1 is g, and σ is a sphere centred on the molecule m with a radius that is the sum of the radii of m and m_1, such that if m_1 comes into contact with

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[3] This is so for the reason mentioned above: the AMC allows correlations between the subset of pairs of molecules that do collide, even if all the pairs fail to exhibit correlations.

[4] This represents the most general case, which is retained for ease of exposition. For identical molecules, one can replace the m_1 with m.

σ, a collision takes place between the two molecules, as depicted in Figure 1. We then define the surface element of area $\sigma^2 d\lambda$ on the sphere σ, which moves with a velocity g relative to the molecule m_1. If the velocity g makes an angle ν with the centre of the surface element $d\lambda$, then in a time interval dt the area $\sigma^2 d\lambda$ traces out an oblique cylinder

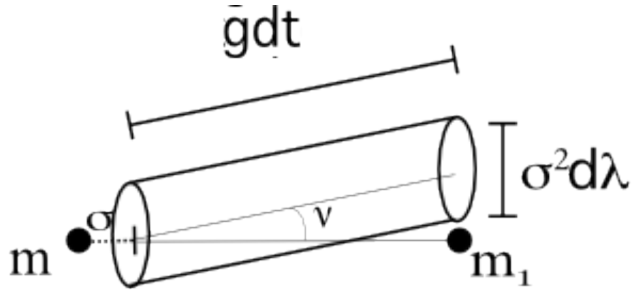

Figure 1: Cylinder of Volume V. If m_1 lies in V, a collision takes place. The cylinder has a base of area $\sigma^2 d\lambda$ and height of $gdt\cos\nu$.

of volume

$$V = \sigma^2 g \cos \nu d\lambda dt\,.$$

If the molecule m_1 is found in this volume, then a collision occurs. In a system, there are $f d\omega$ such volumes, giving a total volume to all such cylinders of $\Phi = V f d\omega$. If the m_1 molecules (in the specified velocity range) are uniformly distributed throughout the system, then the number of such molecules lying within the volume Φ (and hence the number of collisions that take place in dt) will be proportional to the volume Φ, such that the number of collisions that take occur is

$$Z_\Phi = \Phi F d\omega.$$

Boltzmann defines this condition as the condition of molecular disorder (MDC).[5]

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[5] The Ehrenfests (1912) offer a different notion of the assumption of molecular chaos, namely the assumption that, statistically, the actual H-curve fluctuates around the H-curve predicted by the H-theorem, and refer somewhat obliquely to the conception presented above as the Stosszahlansatz.

In a sense this condition is time-symmetric, since it does not specify in what temporal direction (the interval *dt*) the system evolves, so that a system whose velocities are reversed may also be in a state of molecular disorder (and a state evolving towards the intuitive future direction may be molecular ordered). However, it is perfectly possible for the condition to hold asymmetrically; that is, in one temporal direction but not the other. As such, one might understand the MDC as a claim about the instantaneous state of the gas, although such a specification is relative to a chosen temporal direction and a chosen time interval *dt*.

In the LGT, Boltzmann exploits this point to answer the Loschmidt objection. He argues that although the system is molecular disordered in the forward temporal direction, upon reversing the velocities of each molecule, this does not, in itself imply that the system will remain molecular disordered, since under the velocity reversal the MDC need not hold (1896, 58-60).

Does this constitute an advance over the SZA or the usual AMC? As discussed above, the MDC focuses on only those molecules that will be (have been) involved in collisions over the relevant time interval, rather than all pairs of molecules. This condition appears to be one that could (in principle) hold continuously throughout the evolution of a system, whether or not its state resides at a local peak of the H-curve, and thus it remains possible for the H-theorem to predict a monotonic decrease in H. Further, it is an advantage over the SZA that the MDC does not explicitly reference a temporal orientation as a rigidly fixed past or future. Hence, the MDC (and thus the H-theorem) can be applied in either temporal direction in a way that the SZA could not. As such, the MDC picks out a necessary condition for the application of the H-theorem, one that depends on an assumption regarding the microscopic state of the system. This property, claims Boltzmann, will obtain continuously over typical evolutions of the system, but its time-reversed state need not (1898, 325).

In a sense, this is exactly what one would want in looking for a reductive account of the increase in entropy. The account Boltzmann proffers does not explicitly privilege a particular temporal orientation. Conversely, one might argue that the replacement of the SZA by the MDC merely formalises the intuitive rationale for applying the H-theorem in a single temporal direction for non-equilibrium processes: it indicates that, if the velocities of the molecules in a *local* region of space are uncorrelated, they become correlated as the result of collisions and move away from each other so that these correlations are essentially irrelevant to the further evolution of the system (which is what the MDC describes). In the opposite temporal direction, the correlated molecules collide in a way that increases their levels of correlation as the system moves towards higher and higher H-values. Thus, it might seem that we are left with a condition that fails to represent any clear conceptual advantage over the SZA: we still have an assumption that, whether explicitly time-asymmetric or not, simply identifies the direction of a decrease in H. And like the SZA, the putative advantage of the condition lies in its identification of a reductive microscopic condition that underwrites the increase in entropy, though we lack an independent argument for why one should expect this condition to obtain asymmetrically.

4.2 A Second Notion of Molecular Disorder

A second notion of the MDC can also be gleaned from the LGT. Boltzmann (1896) distinguishes between two kinds of disorder in a physical system: molar disorder and molecular disorder. A *molar-ordered* distribution in a gas is one where the values determining the motions of the components of the gas are not uniform across finite regions of the system, such that the velocity distribution in any subvolume of the system is not representative of the system as a whole. Boltzmann does not offer a formal definition of this second conception of ‘molecular disorder’, other than to say that a *molecular-ordered* distribution is one where “groups of two or a small number of molecules can exhibit definite regularities.” (1896, 40) As examples Boltzmann suggests cases where every molecule is moving towards the nearest neighbouring particle or if the velocities of the particles are distributed such that every particle above a certain threshold velocity is surrounded only by slower moving particles. Such a distribution can still be molar-disordered as long as these conditions are uniform throughout the gas. Thus a molar-disordered system can be either molecular-ordered or disordered. However, presumably no molar-ordered system can be molecular-disordered, as any irregularities at the macroscopic level of description must be due to corresponding irregularities at the microscopic level. Thus, the notion of molecular disorder refers to the velocity and spatial distributions in small regions of the gas: those that are important to describing the transport properties of the system.

The definition of MDC offered in the previous section does not jell with the examples of molecular ordered distributions Boltzmann offers. In each of these examples, it is still possible for the formal definition of the MDC to hold; all that is required is that those molecules that find themselves within the volume Φ satisfy the molar-disorder condition; that is, the number of molecules within the volume Φ are representative of the number of molecules with velocities in the specified range in the system as a whole. Since the examples Boltzmann furnishes do not specify how many of these molecules are actually in Φ, they still allow the system to count as molecular disordered (for instance, even if a molecule is surrounded only by slower moving molecules, their velocities may be oriented in such a way as to ensure that the number of molecules lying within Φ satisfy the MDC condition).

Rather, these examples suggest that a molecular ordered distribution is one that depends only on the instantaneous state of the system. Boltzmann implies that a condition of molecular order is specified by looking for velocity correlations among molecules that *may* collide in a localised region of space, rather than the focusing on only those molecules that actually collide. Boltzmann thus suggests that a molecular ordered state is one where “two or a small number of molecules can exhibit definite regularities”.

This focus on the instantaneous state of the system, and away from the treatment of collisions is buttressed by further discussions of the MDC. Although, as we have seen, Boltzmann relies on the possibility that a molecular disordered distribution will not remain so upon a Loschmidt velocity reversal in dealing with the reversibility objection, he makes exactly the opposite claim in 1898 in the second part of LGT. Here, he explicitly adopts an interpretation of molecular disorder that depends only on the existence of correlations in the instantaneous state of the system, independent of a temporal orientation or chosen interval:

> The ordered initial states are not related to the disordered ones in the way that a definite state is to the opposite state (arising from the mere reversal of the directions of velocities), but rather the state opposite each ordered state is again an ordered state.” (1898, 442).

Although this conception of MDC expressly contradicts both the formal definition offered by Boltzmann and numerous claims about molecular disorder made two years earlier, this version of the MDC seems to present at least one significant advantage over the previous incarnation. This conception is not relative to either a temporal interval or a temporal direction, so that merely looking at the instantaneous velocity distribution without such specifications suffices to determine whether the system is or is not in a state of disorder. Thus, anyone who felt there remained a whiff of temporal asymmetry in the first formulation of molecular disorder might feel that this removes any conceptual inadequacy in its formulation. Conversely, Boltzmann does not offer any clear definition of this second notion of molecular disorder, so that it is not clear what this notion amounts to. [6] Further, conceiving of molecular order in this way erases the previous justification for dismissing the Loschmidt objection. If a molecular disordered distribution remains so after a velocity reversal, then Boltzmann cannot maintain that the H-theorem does not apply to the reversed state, and we appear to be in the situation Huang describes; namely, that the MDC can only hold for local peaks in the H-curve.

There is a conceptual gap between the value of H for a system and the characterisation of a system as molecular-ordered or disordered. The H-value of a system depends only on the velocity distribution among the components of the system, independent of their positions. By contrast, the MDC is not limited to a particular velocity distribution (insofar as any velocity distribution can be molecular-disordered), but does make a claim about the spatial distribution of the molecules' velocities. For instance, in terms of the μ-space representation, there may not be any apparent difference between two identical complexions if the system is dense enough such that the molecular-ordering is not apparent on the scale of the size of the cells of the μ-space.[7]

Unlike the SZA, this version of the MDC is a time-symmetric notion that depends only on the instantaneous state of the system. Thus, the MDC is not a diachronic claim about how the distribution changes as the result of collisions. However, whether the condition continues to hold under dynamical evolution is a further issue. Boltzmann claims that one should expect a system to probably remain in a molecular-disordered

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[6] For instance, how many molecules need to be taken into account? How close do the molecules have to be? Are all the molecules that are taken into account weighted equally?

[7] If ordered and disordered complexions were distinguishable, this would a *molar*-ordered distribution, in addition to a molecular-ordered one. Kuhn (1978) also interprets the distinction in this way, though he convincingly argues that Boltzmann, especially in his earlier works, consistently conflates the two.

state if it began in one, and also that if a distribution is initially molecular-ordered, it will almost surely evolve very quickly into a disordered one, at least for all practical purposes. He argues that

> Each molecule flies from one collision to another one so far away that one can consider the occurrence of another molecule, at the place where it collides the second time, with a definite state of motion, as being an event completely independent (for statistical calculations) of the place from which the first molecule came (and similarly for the state of motion of the first molecule). (1896, 41)

In essence, Boltzmann argues that the MDC will hold since, under evolution, the system will behave *as if* it were molecular-disordered (cf. the discussion of Eggarter above). However, he notes “this independence is of course obtained only for a finite number of gas molecules during an arbitrarily long time” (1898, 448), so that despite its appropriateness for the purposes of calculation, a true state of disorder will only be reached in the long run.

5. Molecular Disorder and Probability

The issues raised in section 3, I suggest, are at least tacitly accepted by Boltzmann in the LGT. On the one hand, he is aware that the AMC that has been passed down through the literature is at once a more demanding condition than is necessary to get the H-theorem off the ground, and at the same time not even sufficient for its intended purpose, and the two conceptions of the MDC presented above speak to this sensitivity. At the same time, Boltzmann’s thought was significantly influenced by Loschmidt’s objection, and he strove to develop an argument and/or a justification for the crucial assumption of the H-theorem, the SZA, that does not presume an explicit temporal asymmetry in its formulation. But, at first glance, this appears to be impossible: how can one draw a temporally asymmetric conclusion from solely temporally symmetric assumptions?

There are in fact several moves one can make here. For instance, Frisch (2005) has discussed how an extra-theoretic assumption about the temporal direction of causality has been used to justify discarding advanced solutions to the Maxwell equations, even though formally the theory of classical electromagnetism is temporally symmetric. This sort of move is in principle open to Boltzmann, in that he could appeal to some external justification for the SZA, along the lines of the claim that correlations are only explicable through causal interactions, where the temporal asymmetry of causality is taken as primitive. However, it is clear that Boltzmann did not want to take this route, as he ultimately saw the directionality of time as being something that emerged from his gas theory, rather than explicitly presupposing it.

However, it appears that Boltzmann's actual response follows a similar transcendental line, but relies on a notion of probability rather than causality. In the LGT, he repeatedly uses his condition of molecular disorder as a necessary condition for the use of probabilistic arguments, and sees this as generating the temporal asymmetry of the H-theorem. Further, it appears that this condition serves to link the quantity H with a measure of relative probability of different macrostates, thus connecting the H-theorem with the combinatorial argument. These claims will be detailed below.

Uffink (2006) suggests that in Boltzmann's LGT, the SZA takes the form of an assumption only about the initial state of the gas, and denies a probabilistic understanding of the SZA (where the SZA is understood as a claim about 'most' initial states of a system). Rather, he claims "given Boltzmann's empirical understanding of "the laws of probability"", passages apparently suggesting a dynamical version of the SZA "suggest that Boltzmann thought that, as a *matter of empirical fact*, the assumption would 'almost always' hold, even if the gas was initially far from equilibrium." (50, emphasis added) Indeed, Boltzmann explicitly notes that the fact that one can apply probabilistic notions to the description of physical systems is not unique to the description of gases, as such an assumption is also required for various problems in Astronomy, treatments of viscosity and heat conductivity (1896, 41). In turn, he emphasises that the appropriateness of applying probabilistic concepts to physical systems is something that is in need of empirical justification.[8]

Boltzmann's SZA later becomes transfigured into the assumption that "the velocity distribution is molecular-disordered at the beginning, and remains so. With this assumption, one can prove that H can only decrease and also that the velocity distribution must approach that of Maxwell" (1896, 55). However, according to Boltzmann (at least in 1896), this assumption is violated by Loschmidt's reversibility scenario: rather than the MDC holding throughout the evolution of the system, the system becomes increasingly

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[8] Kuhn (1978, 67) also adopts this reading.

molecular-ordered as it retraces its past states. It is not the H-theorem that is violated by Loschmidt's scenario, but that the MDC, or the claim that the system evolves to molecular-disordered states, does not hold in the reversed case.[9]

Insofar as the H-theorem is intended to provide an explanation of irreversible behaviour, the upshot of this analysis can only show that irreversibility cannot strictly be the rule, but only holds 'almost always', i.e. when the MDC holds. Clearly, this is among the main lessons to take away from Boltzmann's discussion of Loschmidt, but it still leaves us the question with which we began: how is the combinatorial analysis associated with the SZA, AMC or the MDC?

The beginning of an answer to this question comes in looking in greater detail at the work MDC plays in the H-theorem. For Boltzmann, the assumption is more than a claim about the velocity distribution of the system's components, but serves as a necessary condition for the applicability of probabilistic concepts to the kinds of physical systems under consideration. Citing his (1877b) paper, Boltzmann claims that the H-theorem "says simply that through the collisions the velocity distribution of the gas molecules comes closer and closer to the most probable one, as soon as the state is molecular-disordered, and thus the calculus of probabilities is introduced" (1896, 58). A little later on, Boltzmann suggests that Loschmidt's argument "in no way contradicts what was proved in [the derivation of the H-theorem]; the assumption made there that the state distribution is molecular-disordered is not fulfilled here, since after exact reversal of all velocities each molecule does not collide with others according to the laws of probability". Further, Boltzmann refers to this discussion towards the end of the book, pointing out that for the stationary state, "we showed, using the assumption that the molecules move among each other so randomly that the laws of probability can be applied, that it is the only one which satisfies these conditions." (1898, 412)

These claims emphasise that the MDC is neither a hypothesis that emerges from purely mechanical considerations, but also does not admit an interpretation that sees the hypothesis as a strict consequence of probabilistic considerations. Rather, one might view the MDC as a claim about the applicability or appropriateness of probabilistic notions to the description of mechanical systems. Since Loschmidt's objection describes a

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[9] See section 4.1.

molecular-disordered state that will evolve into a molecular-ordered state by reversing the velocity of each molecule, Boltzmann responds that in so doing we would be choosing to "violate intentionally the laws of probability", and proceeds to note that "Kirchhoff also makes the assumption that the state is molecular-disordered in his *definition* of the probability concept." (1896, 41 emphasis added)

In these remarks, we see clearly that Boltzmann does not see the condition of molecular disorder as being either a purely mechanical or a probabilistic concept, *but is a precondition for the applicability of a probabilistic description of the gas' behaviour*. Indeed, elsewhere he remarks that

> [O]ur assumption that in calculating the probability of a particular of encounter of two molecules, the two events that the two molecules are found in certain states can be considered independent, must also be true at all later times. For, according to our assumptions, each molecule moves past a very large number of molecules between successive interactions, so that the state of the gas at the place where the molecule experiences one interaction is completely independent of the state of the gas at the place of the previous interaction, and is determined only by the laws of probability. *Naturally one has to remember that the laws of probability are just that*. (1898, 325, emphasis added)

First, Boltzmann sees the *applicability* of the laws of the probability calculus as something that is to be empirically justified. Although he notes that the MDC finds a place in numerous physical contexts, it should not be assumed that the laws of probability are to be employed without hesitation to any physical system, and thus are not, in themselves, sufficient to justify the application of combinatorial methods. Second, the MDC cannot be understood as a consequence solely of the laws of probability or of Newtonian mechanics. But neither is it an independent assumption that is introduced apart from physical or probabilistic considerations.

In many of the passages cited above, Boltzmann explicitly relies on the H-theorem in his rebuttal to Loschmidt, rather than the combinatorial argument. Boltzmann's (1877b) combinatorial analysis purports to establish the improbability of a Loschmidt-type state, but since it is the content of *the H-theorem* that Loschmidt finds objectionable, the 1877 argument seems to miss the mark. We can still ask *why* it is that the combinatorial analysis should hold if we do not assume the validity of the theorem. The above passages link Boltzmann's probabilistic claims not with the H-theorem generally, but specifically with the MDC. Although it is not the intention here to assess the cogency of this framework as a response to the Loschmidt objection, it is worthwhile to investigate how Boltzmann sees the MDC and the combinatorial argument as linked.

To begin, return to a passage quoted above, where Boltzmann claims the H-theorem "says simply that through the collisions the velocity distribution of the gas molecules comes closer and closer to the most probable one, as soon as the state is molecular-disordered, and thus the calculus of probabilities is introduced" (1896, 58). This passage is somewhat puzzling, as it seems to refer to the most probable state, but at the same time discusses the introduction of probabilities as depending on the system being molecular-disordered. What does Boltzmann mean by the locution 'the most probable state'?

At an intuitive level, it is clear that Boltzmann means the macroscopic equilibrium state of high entropy. But the issue is complicated by the precondition that the state also be molecular disordered in order to introduce probabilities. We can adopt two possible readings of what Boltzmann might mean here:

1. The most probable state is the state corresponding to the highest entropy (greatest number of complexions) in the combinatorial argument, irrespective of whether the state is or is not molecular disordered. In this sense, the meaning of the 'most probable state' is fixed independent of the actual state of the system, whether the laws of probability apply, or more generally the dynamics of the system. The H-theorem then claims that one can only expect the system to move towards this state when the system is molecular disordered.
2. The 'most probable state' only refers when the system is molecular disordered. A molecular ordered state has no 'most probable state', as the application of probabilistic notions to such states is illegitimate.

In the first case, the name 'most probable state' is merely a label for, or rigidly fixes, the equilibrium state, one that adds nothing to its means other than perhaps to emphasise the probabilistic nature of the 2nd law. I take it that this is how this phrase is usually interpreted. However, the 2nd reading also seems possible, and is worth exploring.

The issue relates to the "twofold meaning of the quantity H" alluded to in the introduction. On the one hand, Boltzmann claims that H has a physical meaning, presumably alluding to its role as a measure of the entropy (up to a constant). In its mathematical guise, H serves as a measure of the relative probability of different states, with the state of minimal H being the "most probable state". [10] To speak in the same breath of a system evolving to the 'most probable state' once a system is molecular

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[10] There is a full section of the LGT entitle "the mathematical meaning of the quantity H", though Boltzmann never specifies what is meant by this. However, the section describes the combinatorial argument.

disordered links the H-theorem to the combinatorial argument, for it claims that the condition required for the H-theorem to hold is the very same condition needed to apply the combinatorial argument. Boltzmann seems to explicitly endorse this reading in claiming that

> "The fact that in nature the entropy tends to a maximum shows that for all interactions (diffusion, heat conduction, etc.) of actual gases the individual molecules behave according to the laws of probability in their interactions, or at least that the actual gas behaves like the molecular-disordered gas which we have in mind.
>
> The second law is thus found to be a probability law. We have of course proved this only in a special case, in order not to make it too difficult to understand because of too much generality. Moreover, the proof that for a gas of arbitrary volume Ω the quantity ΩH – and for several gases the quantity Σ ΩH – *can only decrease through collisions, and thus is to be considered as a measure of the probability of states*, was only hinted at." (1896, 74-75, emphasis added)

Whether or not it makes sense to apply the honorific 'most probable state' to a system that is molecular ordered, Boltzmann appears to claim that the justification for both the H-theorem and the combinatorial argument lies in the molecular disordered state of the system.

This is noteworthy since it appears to link the condition of molecular disorder to the combinatorial argument in a way that is not to be found in Boltzmann's original replies to Loschmidt, in the sense that the SZA is not invoked in any way to justify the argument. As an historical matter, this is easily explicable: Boltzmann was not aware of the importance of the SZA in his proof of the H-theorem. In any case, to invoke the SZA as a justification for the combinatorial argument would simply beg the question against Loschmidt's worry, given its time asymmetric nature. However, we see in 1896 Boltzmann explicitly links the validity of the combinatorial argument to the MDC, which serves both as the justifying assumption needed to underwrite the H-theorem and the application of the laws of probability.[11]

6. Conclusion

This paper has examined Boltzmann's conception of molecular disorder, and proposed two alternative definitions of the condition based on his LGT. Although little effort has been made to assess the cogency or usefulness of these conceptions, I have argued that both offer significant differences (and potential advantages) to the usual understandings of the Stosszahlansatz and the Assumption of Molecular Chaos that one

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[11] Although this link is made fairly explicit, I can find no argument in Boltzmann as to why it should hold.

finds in the literature. A more detailed examination of these notions of the MDC will be left to further work.

Beyond this, it has been argued that Boltzmann saw the MDC as being a sort of necessary condition for the use of the probability calculus in describing the behaviour of physical systems. Drawing on this claim, Boltzmann uses the violation of the MDC in Loschmidt's reversibility objection as grounds for dismissing the objection as a counterexample to the H-theorem, and further argues that the combinatorial argument can only apply when the MDC obtains, since it both justifies the application of the combinatorial argument and gives meaning to the phrase 'the most probable state'.

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