

## On the H-Theorem for Polyatomic Gases

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The H-theorem for a classical gas of polyatomic molecules of arbitrarily complex structure is examined. A simple use of time reversal invariance of the equations of dynamics is used to circumvent the objections which were raised by Lorentz against Boltzmann's proof (nonexistence of inverse collisions).

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**KEY WORDS:** H-theorem; polyatomic gases; Boltzmann equation; kinetic theory.

### 1. INTRODUCTION

Since the publication, in 1872, of the famous memoir of Boltzmann,<sup>(1)</sup> containing, as one of its many remarkable features, the proof of the H-theorem for monatomic gases, the debate on the meaning of this result has gone on and we can say that even today one can find scepticism about the meaning of this basic contribution of Boltzmann's to nonequilibrium statistical mechanics.<sup>(2)</sup>

It is even more surprising, therefore, to find that the extension of the H-theorem to a gas whose molecules are arbitrarily complex structures, which was proposed by Boltzmann in the same basic paper<sup>(1)</sup> and subsequently criticized by Lorentz,<sup>(3)</sup> is not usually discussed in treatises on kinetic theory, even those which deal with explicit models for polyatomic molecules,<sup>(4)</sup> with the notable exceptions of Boltzmann's "Lectures"<sup>(5)</sup> and Tolman's book.<sup>(6)</sup>

As is well known, Lorentz's objection to Boltzmann's proof is based on the fact that one cannot expect to find any inverse collision for an arbitrarily chosen collision, with the exception of molecules having a spherically symmetric interaction. We underline the circumstance that it is not the geometric shape of the molecules which matters but rather the

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details of the interaction, as shown by the case of rough spherical molecules.<sup>(7,8,4)</sup>

Boltzmann tried hard to fight with the objections of Lorentz. He carefully distinguished between initial and final, time reversed and corresponding "constellations," finally arriving at the so-called cycle proof of the H-theorem.<sup>(9,5,6)</sup> It is not clear, however, that this argument really proves something, and as recently as 1972, G. E. Uhlenbeck<sup>(10)</sup> stated that he had some doubts about these generalizations. He then suggested a way of escape in the quantum treatment of the collisions, as developed by L. Waldmann<sup>(11,12)</sup> and R. F. Snider.<sup>(13)</sup> As a matter of fact the possibility of finding a proof of the H-theorem for polyatomic gases in quantum mechanics as a consequence of the unitarity of the scattering matrix had been pointed out as early as 1952 in a paper by Stueckelberg<sup>(14)</sup> and described later in connection with a quantum Boltzmann equation by Waldmann.<sup>(15)</sup>

It is the purpose of this paper to point out that there is a proof of the H-theorem for a gas of purely classical molecules with arbitrarily complex structure. The starting point will be the reciprocity relation for the scattering probability; the latter holds because of the time-reversible character of the equations of the dynamics.

## 2. BASIC EQUATIONS

We shall deal with molecules described by a set of variables, which will include the position vector  $\mathbf{x}$  and other variables which will be collectively denoted by  $\mathbf{p}$  ( $\mathbf{p}$  will be a vector in an  $n$ -dimensional space); the latter will include, e.g., velocity and angular velocity or angular momentum.

The distribution function  $f = f(\mathbf{x}, \mathbf{p}, t)$  will satisfy an evolution equation of the form

$$\frac{\partial f}{\partial t} + \mathbf{P} \cdot \frac{\partial f}{\partial \mathbf{p}} = \int \int \int [f(\mathbf{x}, \mathbf{p}', t)f(\mathbf{x}, \mathbf{p}_*, t)W(\mathbf{p}', \mathbf{p}_* \rightarrow \mathbf{p}, \mathbf{p}_*) - f(\mathbf{x}, \mathbf{p}, t)f(\mathbf{x}, \mathbf{p}_*, t)W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}_*)] d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}_* \quad (2.1)$$

where  $\mathbf{P}$  is a  $n$ -dimensional vector which is assigned when the causes different from collisions deviating the molecules from rectilinear paths are given through the equation of collision-free motion:

$$\dot{\mathbf{p}} = \mathbf{P}(\mathbf{x}, \mathbf{p}) \quad (2.2)$$

In Eq. (2.1)  $\mathbf{p}_*$  denotes the variables of the partner of  $\mathbf{p}$  in a collision,  $\mathbf{p}'$ ,  $\mathbf{p}'_*$  the variables of two molecules which end up in the state  $\mathbf{p}$  and  $\mathbf{p}_*$ , respectively, at the end of a collision. The transition "probability"  $W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*)$  is essentially the differential cross section multiplied by relative

speed, and in fact one has

$$\int \int W(\mathbf{p}', \mathbf{p}'_*; \mathbf{p}_*) d\mathbf{p}' d\mathbf{p}'_* = |\xi - \xi_*| \sigma_t \tag{2.3}$$

where  $\sigma_t$  is the total cross section. The latter could, in principle, depend on the variables  $\mathbf{p}$  and  $\mathbf{p}_*$ ; as a matter of fact we shall assume that it does not, by a sort of trick. First, we shall assume that no interaction takes place when the molecules are separated by more than a certain distance  $r_0$  (finite range interaction). We can then assume that  $\sigma_t$  is exactly  $\pi r_0^2$  provided we allow the presence of no-scattering events in  $W$ : in other words if for certain values of  $\mathbf{p}'$ ,  $\mathbf{p}'_*$  there is no interaction between the molecules even at a distance smaller than  $r_0$ , we shall consider  $W$  different from zero there and actually proportional to a delta function ensuring that no change takes place during the “collision.” This convention will notably simplify our treatment. The case of infinite range interaction can be dealt with, if desired, by a limiting procedure on the results which will be established here.

We remark that the time reversibility of the equation of motion implies that there is a transformation  $\mathbf{p} \rightarrow \mathbf{p}^-$  (typically  $\mathbf{p}^- = -\mathbf{p}$ ) such that

$$W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) = W(\mathbf{p}^-, \mathbf{p}_*^- \rightarrow \mathbf{p}'^-, \mathbf{p}'_*^-) \tag{2.4}$$

This property will be called as usual “reciprocity.” In addition the transformation from  $\mathbf{p}$  to  $\mathbf{p}^-$  is measure preserving. In the case of a perfectly spherical interaction, the additional property

$$W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) = W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) \tag{2.5}$$

called detailed balance, applies.

Use of Eq. (2.5) would allow a proof of the H-theorem by a word-by-word repetition of the proof holding for the monatomic gas. If Eq. (2.5) fails, then one usually invokes Boltzmann’s argument based on the assumption of “closed cycles of collisions,”<sup>(9,5,6)</sup> which many authors have found difficult to follow. The main feature of the proof, however—viz., that many collisions have to be lumped together—is the key to the proof in the quantum case as well as to the proof for the classical equation which we are presenting here. We integrate both sides of Eq. (2.4) with respect to  $\mathbf{p}, \mathbf{p}_*$  to find

$$\begin{aligned} \int \int W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) d\mathbf{p} d\mathbf{p}_* &= \int \int W(\mathbf{p}^-, \mathbf{p}_*^- \rightarrow \mathbf{p}'^-, \mathbf{p}'_*^-) d\mathbf{p} d\mathbf{p}_* \\ &= \int \int W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}'^-, \mathbf{p}'_*^-) d\mathbf{p} d\mathbf{p}_* \end{aligned} \tag{2.6}$$

where we have changed the integration variables from  $\mathbf{p}, \mathbf{p}_*$  to  $\mathbf{p}^-, \mathbf{p}_*^-$  and then suppressed the minus superscript, which is no longer needed ( $d\mathbf{p} d\mathbf{p}_*$

$= d\mathbf{p}^- d\mathbf{p}_*^-$ ). The last integral in Eq. (2.6) is nothing else, according to Eq. (2.3), than

$$|\xi'^- - \xi_*^-| \sigma_t = |\xi' - \xi_*| \sigma_t = \iint W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* \quad (2.7)$$

where  $\xi'^- = -\xi'$  and  $\xi_*^- = -\xi_*$  and the constancy of  $\sigma_t$  have been used. Equations (2.6) and (2.7) together give

$$\iint W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) d\mathbf{p} d\mathbf{p}_* = \iint W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* \quad (2.8)$$

This is a basic new relation which will be used in the next section to prove the H-theorem. The importance of a relation such as Eq. (2.8) was stressed by Waldmann, who, guided by the analogous relation in the quantum case, wrote it for the first time in the particular case of a gas of classically rotating linear molecules.<sup>(16)</sup> He did not present, however, any proof of Eq. (2.8) but stated that "one must get the (purely mechanical) normalization property" expressed by Eq. (2.8). As a possible proof he seems to hint at a complete calculation with the simplifying assumption of "averaging over all possible phase angles before and after collision." This averaging, though practically convenient in order to avoid the use of ignorable coordinates (in the absence of external electric fields), is not required in our direct proof. According to our approach, Eq. (2.8) is a general property following from the time reversibility of the microscopic equations of motion.

### 3. PROOF OF THE H-THEOREM FOR POLYATOMIC MOLECULES

It is now a simple matter to prove Boltzmann's lemma, according to which if we let

$$Q(f, f) = \iint [f' f'_* W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) - f f_* W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*)] d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* \quad (3.1)$$

then

$$\int \log f Q(f, f) d\mathbf{p} \leq 0 \quad (3.2)$$

$f', f'_*, f_*$ , in Eq. (3.1) denote, as usual, the distribution function  $f$  having, as  $p$ -argument,  $\mathbf{p}', \mathbf{p}'_*, \mathbf{p}_*$ , respectively. This lemma is the basic prerequisite for the proof of the H-theorem: if Eq. (3.2) holds, then the proof develops in the traditional way.<sup>(1,4,5,17,18)</sup>

In fact we multiply Eq. (3.1) by  $\log f$  and integrate, we obtain

$$\int \log f Q(f, f) d\mathbf{p} = \frac{1}{2} \int \int \int \int ff_* \log \left( \frac{f'f'_*}{ff_*} \right) W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* \quad (3.3)$$

This relation can be obtained by standard manipulations, i.e., suitable changes of variables and labels and does not involve any use of the properties of  $W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*)$ . Equation (3.3) does not permit to use the standard argument for proving the H-theorem; to use the latter one should add to Eq. (3.3) the same equation after having interchanged primed and unprimed variables and use Eq. (2.5), which, however, does not hold in general.

At this point we use a mathematical trick which seems to have been suggested by Pauli<sup>(14)</sup> in connection with the quantum mechanical proof. Along with the identity expressed by Eq. (3.3) we consider the other identity

$$\int f'f'_* W(\mathbf{p}', \mathbf{p}'_* \rightarrow \mathbf{p}, \mathbf{p}_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* = \int ff_* W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* \quad (3.4)$$

which follows from a change of labels and expresses conservation of mass. In the left-hand side of Eq. (3.4) we can transform the integral over the unprimed variables according to Eq. (2.8) to obtain

$$\int f'f'_* W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* = \int ff_* W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* \quad (3.5)$$

or equivalently

$$\frac{1}{2} \int ff_* \left( \frac{f'f'_*}{ff_*} - 1 \right) W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* = 0 \quad (3.6)$$

Hence we can subtract the integral appearing in the left-hand side of Eq. (3.6) from the right-hand side of Eq. (3.6) without changing anything. We obtain

$$\int \log f Q(f, f) d\mathbf{p} = \frac{1}{2} \int \int \int \int ff_* \left[ \log \frac{f'f'_*}{ff_*} - \left( \frac{f'f'_*}{ff_*} - 1 \right) \right] \times W(\mathbf{p}, \mathbf{p}_* \rightarrow \mathbf{p}', \mathbf{p}'_*) d\mathbf{p} d\mathbf{p}_* d\mathbf{p}' d\mathbf{p}'_* \quad (3.7)$$

Since  $f, f_*, W$  are positive and

$$\log x - (x - 1) \leq 0 \quad (3.8)$$

the equality sign holding if and only if  $x = 1$ , we conclude that inequality (3.2) is proved, the equality sign applying if and only if (almost everywhere):

$$f'f_* = ff_* \quad (3.9)$$

This relation, as is well known, leads to the equilibrium distribution ( $\log f$  must be a linear combination of the collision invariants).

#### 4. CONCLUDING REMARKS

Interest in the classical kinetic theory of polyatomic gases has revived since the theoretical work of Kagan and co-workers<sup>(19,20)</sup> and the rediscovery of the Senftleben–Beenakker effect by Beenakker and co-workers.<sup>(21)</sup> Usually, however, theoretical considerations have been based on the quantum mechanical version of the Boltzmann equation, the so-called Boltzmann–Waldmann–Snider equation, even when quantum aspects were clearly irrelevant. This attitude was partly justified by the feeling that clarification of some aspects of the classical model were required. Recently proofs were offered of the fact that one can pass to the limit  $\hbar \rightarrow 0$  in the quantum equation to obtain perfectly reasonable nonlinear<sup>(22)</sup> or linearized<sup>(23)</sup> classical equations. The latter paper also supplies error estimates when quantum effects are neglected.

In this paper we have offered a proof of the H-theorem for the classical Boltzmann equation for polyatomic molecules. This proof avoids all the difficulties which Boltzmann and subsequent writers met in discussing the theorem in the case of a nonspherical interaction. It is hoped that this analysis will dissipate some suspicion about the use of classical models for the description of gases, whose molecules have a complex structure.

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