A TREATISE ON THE KINETIC THEORY OF GASES

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HENRY WILLIAM WATSON

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ON THE

KINETIC THEORY OF GASES

BY

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PREFACE.

THE idea of a Kinetic Theory of Gases originated with J. Bernouilli about the middle of the last century, but the first establishment of the theory on a scientific basis is due to Professor Clausius.

During the last few years the theory has been greatly developed by many physicists, especially by Professor Clerk Maxwell in England and Professor Clausius and Dr. Ludwig Boltzmann on the Continent; and although still beset by formidable difficulties, it has succeeded in explaining most of the established laws of gases in so remarkable a manner as to render it well worthy of the attentive consideration of scientific men.

My great object in the following short treatise is to make the existing state of the theory more widely known by presenting some of the scattered memoirs of the writers I have mentioned in a systematic and continuous form, in the hope that mathematicians may be induced to turn their attention to the theory, and thus assist in removing, if possible, the obstacles which yet remain in the way of its complete establishment.

For the most part I have followed the method of treatment adopted by Dr. Ludwig Boltzmann in some very interesting memoirs contributed by him to the

Transactions of the Imperial Academy of Vienna,* but in some cases I have varied this treatment for the sake of greater conciseness or greater generality.

Thus, in place of Dr. L. Boltzmann's conception of a molecule as a collection of mutually attracting particles, I have substituted the more general conception of a material system possessing a given number of degrees of freedom, that is to say, a given number of generalised coordinates.

Again, in the deduction of the second law of Thermodynamics from the results of the Kinetic Theory, I felt some difficulty in following Dr. Boltzmann's reasoning, and I originally proposed to substitute for it a demonstration of my own, free from what appeared to me to be the obscurities of Dr. Boltzmann's reasoning, but applicable only to the case in which there were no intermolecular actions. My friend Mr. S. H. Burbury, formerly fellow of St. John's College, Cambridge, to whom I communicated my difficulties, has invented an unexceptionable proof applicable to all cases, which he published last January in the London, Edinburgh, and Dublin Philosophical Magazine, and with his permission I have adopted this proof in the following treatise.

To Professor Clerk Maxwell I am indebted for much kind assistance, and especially for access to some of his manuscript notes on this subject, from which I have taken many valuable suggestions.

H. W. WATSON.

BERKSWELL RECTORY,
COVENTRY, *Sept.* 17, 1876.

* Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien, Band 63, 1871, und Band 66, 1872.

INTRODUCTION.

The Kinetic Theory of Gases is based upon the conception of an infinitely large number of molecules in motion in a given space with velocities of all degrees of intensity and in all conceivable directions. These molecules, as will be explained in the course of the following treatise, may sometimes be regarded as smooth spheres, in which case we shall only have to consider the motion of translation of the centre of mass of each of them, or they may be regarded as bodies of any form capable of any number of internal vibrations. It is clear that the individual molecules in such a system must be continually acting upon each other, either in the way of collision, like the mutual impacts of elastic spheres, or else in the more gradual way of mutual attraction and repulsion; such actions are called encounters.

It is easy to see that if encounters take place among a great number of molecules, their velocities, even if originally equal, will become unequal, for, except under conditions which can be only rarely satisfied, two molecules having equal velocities before their encounter will have unequal velocities after such encounter. Now, as long as we have to deal with only two molecules, and have all the data of an encounter given us, we can calculate the result of their mutual action; but when we have to deal with millions of molecules, each of which has millions of encounters in a second, the complexity of the problem seems to shut out all hope of a legitimate solution.

We are obliged therefore to abandon the strictly kinetic method and to adopt the statistical method.

According to the strict kinetic or historical method as applied to the case before us, we follow the whole course of every individual molecule. We arrange our symbols so as to be able to identify every molecule throughout its motion, and the complete solution of the problem would enable us to determine at any given instant the position and motion of any given molecule from a knowledge of the positions and motions of all the molecules in their initial state.

According to the statistical method, the state of the system at any instant is ascertained by distributing the molecules into groups, the definition of each group being founded on some variable property of the molecules. Each individual molecule is sometimes in one of these groups and sometimes in another, but we make no attempt to follow it; we simply take account of the number of molecules which at a given instant belong to each group.

Thus we may consider as a group those molecules which at a given instant lie within a given region of space. Molecules may pass into or out of this region, but we confine our attention to the increase or diminution of the number of molecules within it. Just as the population of a watering-place, considered as a mere number, varies in the same way whether its visitors return to it season after season, or whether the annual gathering consists each year of fresh individuals. Or we may form our group out of those molecules which at a given instant have velocities lying within given limits. When a molecule has an encounter and changes its velocity, it passes out of one of these groups and enters another; but as other molecules are also changing their velocities, the number of molecules in each group varies little from a certain average value.

We thus meet with a new kind of regularity, the regularity of averages, a regularity which, when we are dealing with millions of millions of individuals, is so unvarying that we are almost in danger of confounding it with absolute uniformity.

Laplace, in his Theory of Probability, has given many examples of this kind of statistical regularity, and has shown how this regularity is consistent with the utmost irregularity among the individual instances which are enumerated in making up the results.*

These observations must be borne in mind in interpreting the definitions laid down and the results arrived at in the Kinetic Theory of Gases.

Thus, to refer to the illustrations already given, we shall prove that the number of molecules lying within a certain region of space, or the number of molecules having their velocities within certain limits differing by some finite quantity, is in each case a number bearing some finite ratio to the total number of molecules in the mass under consideration, and therefore infinitely large. But these results are to be interpreted as average results. We do not assert by them, nor are we capable of proving, that at any given instant there is one single molecule satisfying either of the required conditions, that is, comprised within either of the contemplated groups.

So, again, the density of the region in the neighbourhood of any point is defined as the limit of the quotient of the number representing the aggregate masses of the molecules within any volume containing the point, to the number representing that volume, when the volume is indefinitely diminished. In interpreting this definition two things must be remembered. In the first place, according to what has been said just now, we do not assert and cannot prove that there is, as a matter of fact, any particular number of molecules within the volume containing the given point, at any given instant; and in the second place, supposing we could prove that the number of molecules within the volume was thus accurately determined, yet even so there could be no

* MS. notes by Professor Clerk Maxwell.