A TREATISE ON THE KINETIC THEORY OF GASES

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BY

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PREFACE.

My object in the following treatise is to apply to the Kinetic Theory of Gases a method of analysis different from that generally employed. It has been treated always on a certain fundamental assumption, namely, that the molecules of a gas are, as regards their relative motion, *independent* of one another. As a consequence, we may say as the expression, of that independence, the law of distribution of momenta assumes the exponential form ϵ^{-hQ}, and, so far as concerns translation velocities,

$$Q = \Sigma m (u^2 + v^2 + w^2),$$

m being mass, and u, v, w component velocities. From this independence and from this form of Q are deduced Boltzmann's theorems, namely the H theorem, and that of the equality of mean kinetic energy for each degree of freedom.

I propose to give to Q the more general form of a quadratic function, namely

$$Q = \Sigma m (u^2 + v^2 + w^2) + \Sigma\Sigma b (uu' + vv' + ww').$$

Here b is a negative function of the distance r at the instant considered between the two molecules whose velocities are u, u', etc., which function is inappreciable except for very small values of r. I shall endeavour to prove in Chapters IV., V. that without the b coefficients the motion cannot be stationary. It has been proved abundantly that, *assuming the independence*, the motion *is* stationary with the usual form of Q. I question the axiom, not the demonstration.

The consequence of attributing to Q the proposed new form is, that molecules near to each other have on average a motion in the same direction. They tend to form streams. That result, if it can be established, is worth investigation.

For ordinary gases under ordinary conditions the b coefficients are probably very small, and their effect negligible in such investigations as those of Tait and Boltzmann concerning diffusion, viscosity, etc. But I think that the law ϵ^{-hQ} in its altered form will express the state of the system without restriction as to density, except as follows. A physical limit there must be, when the gas liquefies under pressure, if not before. For it will not be contended that the distribution of momenta among the molecules of the liquefied gas is represented by the same exponential form as in the gaseous condition. An analytical limit there is, when Q in its altered form ceases to be necessarily positive, that is when the determinant of the coefficients ceases to be positive. It can be shown that this determinant does diminish as density increases, or temperature diminishes. But I have not calculated its value. It is therefore no more than a conjecture, though perhaps a plausible conjecture, that the vanishing of the determinant may coincide with the physical change in the substance.

It appears to me that the law of equality of mean kinetic energy for each degree of freedom cannot be reconciled with my proposed form of Q; that in fact the law holds only for the limiting case of a very rare gas.

It is no light thing to question a conclusion maintained by Boltzmann, if indeed he does maintain this conclusion for all substances, or for all gases irrespective of density. I can but state the objections to this theorem, and to a certain aspect of the H theorem, as they appear to me. The reader will judge what weight is to be attributed to them.

S. H. BURBURY.

10 *May*, 1899.

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CHAPTER I.

OUTLINE OF THE THEORY.

1. A GAS according to the Kinetic Theory consists of a great number of molecules in rapid motion. And the object of the theory is to explain on this hypothesis certain of the physical properties of gases.

Any quantity of gas which can be isolated for the purpose of experiments is to be regarded as containing a number of molecules practically infinite. It is not possible to control or to observe the motions of individual molecules. But the theory assumes that such motion is subject to the usual dynamical laws. Also that if the gas, as an aggregate of molecules, be at rest, no dissipation of energy takes place.

2. A molecule may consist of one or more than one atom according to the chemical constitution of the substance to which it belongs. It may be that hereafter we shall be able to explain on dynamical principles the chemical relations of atoms as constituent parts of a molecule, and of molecules *inter se*. And some progress has been made in this direction. At present the theory is concerned not with the chemical properties, but with those properties of gases which may change without any change taking place in the chemical composition of the gas: for instance, density, pressure, and temperature. And as depending on these latter, it is concerned with the phenomena of viscosity, diffusion, and conduction of heat or electricity.