

7. A PROOF OF MAXWELL'S LAW, THE PRINCIPAL PROPOSITION IN THE KINETIC THEORY OF GASES

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1. In the sixties of the nineteenth century, the old inconsistent and vague notions of the molecules of the gases were superseded by a positive theory (*Maxwell, Boltzmann*), and the head stone of this theory is the Maxwellian Law of Distribution. This came to be the initiation of an entirely new view of, and working method in Physics, *viz.* the view and method based upon the Theory of Probabilities generally known, of late years, as the "Statistical Method". For many years it had to face the misapprehension, indifference, and antagonism of a mighty school of natural scientists; but then one must admit that this aversion has been done away with in the present century, and the new methods are now, undoubtedly, recognized as the only serviceable with respect to a steadily growing number of phenomena, including the electrical. It is now rather obvious that the old manner of dealing with problems such as the principles of the Theory of Heat is not satisfactory, and that paths leading to better comprehension can be found. A concurrent of the change that has occurred was, of course, the experimental investigations that gradually banished any doubt as to the actual existence of the molecules as individuals, and their possession — to some extent, at least — of the properties upon which the theories were based (*Christiansen, Knudsen, Perrin*, and others). It is a matter of course that this development is not only physically significant; it must interest, also, those who work with the Theory of Probabilities and its applications on the whole, as indicated by the literature of recent years.

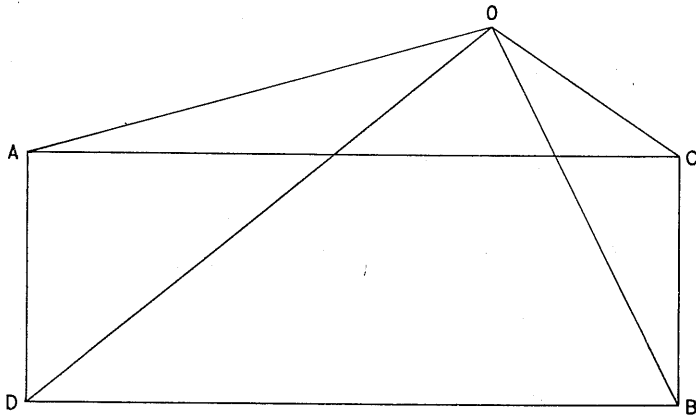
It admits of no doubt whatever that many people must have wanted to partake of the understanding thus attained. One might, perhaps, expect to find in the more recent manuals on physics, if not a thorough discussion of problems belonging here (such as diffusion, currents in gases, thermal conduction, the two specific heats) — which questions, by the way, have as yet hardly been treated in a quite unchallengeable manner, on the given presuppositions —, then at least a simple and clear proof of the Maxwellian law of distribution. Any such proof is seldom or never

to be found, however; even special works on the Kinetic Theory are of no avail in this respect. I have therefore put down in writing the following proof which is based upon the very simplest and most well-known mathematical and mechanical theorems (I have not even used, *e. g.*, the Principle of Energy); consequentially, I believe, the characteristics of the reasoning stand a better chance of being recognized.

2. *Presuppositions about the Nature of the Molecules and the Effects of the Collisions.*

The molecules are all alike; they are hard, smooth, elastic spheres; and they are homogeneous or, if you like, their distribution of mass is mechanically equivalent to that of a homogeneous body. They move in a large space, with constant velocity along straight lines so long as no collisions occur. As usual, the velocity may be represented by a vector going out from the centre of the sphere. We make no special presuppositions as to the size of the spheres in proportion to the distances. It may be advantageous to replace the three-dimensional domain (space) which we are dealing with, strictly speaking, with a two-dimensional one (a plane); this would make the drawing of figures and the formulating of the proof slightly easier, although everything essential will remain the same in both cases.

The laws governing collision of elastic spheres are well-known; already *Huygens* set forth the main principles, though only for the uni-dimensional problem of central impact. Let us assume that we know the two velocities OA and OB before the impact; at this occasion it will be convenient to plot them from the point of contact O of the spheres. Further, we know the direction of thrust: the spheres being smooth, this is identical with



the radii to the point of contact at the moment of the impact. The impact will change OA to OC , and OB to OD . For the determination of C and D we have: AC is equal to, and parallel with, BD (but of opposite direction), and both are parallel with the direction of thrust; further, the quadrangle $ACBD$ is (not only a parallelogram, but also) a rectangle. That this is the case can be proved as follows: — During the first period of the elastic impact, *i. e.* while the compression is increasing, the end of the one vector will move from A to M , M being the middle point of AC ; likewise, the end of the other vector will move from B to N , N being the middle point of BD . The relative velocity before the impact was AB ; now it is MN . But this first period will cease when the relative velocity is at right angles to the direction of thrust; then the second period begins during which the spheres move away from each other, and it lasts until the state of contact is discontinued.

It should be remembered that no rotation is involved, according to the presuppositions; either the spheres do not rotate at all, or else the rotations will remain unchanged even during the collision.

3. Concerning the Initial State.

We will suppose that the state of the molecules (*i. e.* their position and velocity) at a certain time is as follows. The molecules are assumed to be distributed quite accidentally in the plane (or, strictly speaking: space) concerned, independent of each other, with the one exception that no two molecules can occupy the same place partly or wholly. As mentioned before, the velocity of an arbitrary molecule shall be represented by a vector going out from the molecule. We can consider an infinitely small area (strictly speaking, a volume) around a point situated at a distance r from the molecule in some direction or other. We let the probability of a velocity, the vector of which has its terminal point in this small area, be proportional to e^{-kr^2} and to the magnitude of the area but independent of the direction. Another, more exact way of expressing the same is to say that the probability density in this portion of the plane and e^{-kr^2} are in proportion. The probability density (also sometimes called the point probability) is defined as the limit value of the ratio between the probability corresponding to a certain area and the magnitude of the said area as both converge towards zero. The precise "physical" significance of the quantity k need not be considered here. — The state thus described may be called the normal or Maxwellian state. Now the problem is to prove that this state is in "statistical equilibrium", *i. e.* that conditions as a whole will not cease to be as described above, in spite of the changes in the separate molecules caused partly by the rectilinear motion, partly

by the collisions. For, having proved this, we shall also have proved Maxwell's law.

4. The Proof.

To begin with, it is obvious that the usual rectilinear motion will not discontinue the Maxwellian state. Let us now consider a collision which is to take place in the point O . The initial velocities are $OA = a$ and $OB = b$, and the direction of thrust is given.

Now, we want to find the probability (more exactly, the probability density) that a collision of this kind will occur in the near future; later, we shall have to let both A and B traverse the entire plane. Pursuant to the preceding, and in accordance with the theorem about multiplication of probabilities, the expression for the sought-after probability must contain, as factors, firstly the expression

$$e^{-ka^2} \cdot e^{-kb^2} = e^{-k(a^2 + b^2)};$$

secondly, the relative or reciprocal velocity $AB = p$; and finally, cosine of the angle BAC between the said velocity and the direction of thrust; for, when the spheres are rather near to each other — which is the only case we need consider — and moving towards each other, $p \cdot \cos \angle BAC$ will be the velocity with which the spheres are approaching each other. Consequently, this quantity will express the permissible distance between the spheres if we make it a condition that the collision take place within a certain, narrow time limit.

We will now pass on to a consideration of the reversed collision, *i. e.* the direction of thrust is the same as before but the initial velocities are OC and OD , and — as is at once obvious — the final velocities are OA and OB ; we can here use the same drawing as before. In order to prove that the two probabilities are identical, we use the three equations:—

$$a^2 + b^2 = c^2 + d^2 \tag{1}$$

$$AB = CD \tag{2}$$

$$\angle BAC = \angle CDB \tag{3}$$

(2) and (3) are at once obvious. The equation (1) is obtained by a simple elementary-geometrical demonstration (an auxiliary line from O at right angles to the two sides of the rectangle; the Pythagorean proposition); it might also be obtained from the principle of energy, but that would evidently be making a detour.

We will now divide the whole plane into small squares (or, if you like, rectangles), the sides of which are partly parallel to, and partly at right angles to the direction of thrust. If A is situated inside such a square

and B inside another, then C and D will be situated inside a similar pair of squares. We have now proved the existence of statistical equilibrium although only as far as the impacts hereto corresponding are concerned. But, as we can now proceed to choose a new pair of squares for A and B , and so on, and so forth, until there are no more possibilities, we have herewith proved Maxwell's theorem.