

IV. *On the Dynamical Theory of Gases.* By J. CLERK MAXWELL, F.R.S. L. & E

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THEORIES of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules.

In certain applications of mathematics to physical questions, it is convenient to suppose bodies homogeneous in order to make the quantity of matter in each differential element a function of the coordinates, but I am not aware that any theory of this kind has been proposed to account for the different properties of bodies. Indeed the properties of a body supposed to be a uniform *plenum* may be affirmed dogmatically, but cannot be explained mathematically.

Molecular theories suppose that all bodies, even when they appear to our senses homogeneous, consist of a multitude of particles, or small parts the mechanical relations of which constitute the properties of the bodies. Those theories which suppose that the molecules are at rest relative to the body may be called statical theories, and those which suppose the molecules to be in motion, even while the body is apparently at rest, may be called dynamical theories.

If we adopt a statical theory, and suppose the molecules of a body kept at rest in their positions of equilibrium by the action of forces in the directions of the lines joining their centres, we may determine the mechanical properties of a body so constructed, if distorted so that the displacement of each molecule is a function of its coordinates when in equilibrium. It appears from the mathematical theory of bodies of this kind, that the forces called into play by a small change of form must always bear a fixed proportion to those excited by a small change of volume.

Now we know that in fluids the elasticity of form is evanescent, while that of volume is considerable. Hence such theories will not apply to fluids. In solid bodies the elasticity of form appears in many cases to be smaller in proportion to that of volume than the theory gives\*, so that we are forced to give up the theory of molecules whose displacements are functions of their coordinates when at rest, even in the case of solid bodies.

The theory of moving molecules, on the other hand, is not open to these objections. The mathematical difficulties in applying the theory are considerable, and till they are surmounted we cannot fully decide on the applicability of the theory. We are able, however, to explain a great variety of phenomena by the dynamical theory which have not been hitherto explained otherwise.

The dynamical theory supposes that the molecules of solid bodies oscillate about their

\* [In glass, according to Dr. EVERETT'S second series of experiments (1866), the ratio of the elasticity of form to that of volume is greater than that given by the theory. In brass and steel it is less.—March 7, 1867.]

positions of equilibrium, but do not travel from one position to another in the body. In fluids the molecules are supposed to be constantly moving into new relative positions, so that the same molecule may travel from one part of the fluid to any other part. In liquids the molecules are supposed to be always under the action of the forces due to neighbouring molecules throughout their course, but in gases the greater part of the path of each molecule is supposed to be sensibly rectilinear and beyond the sphere of sensible action of the neighbouring molecules.

I propose in this paper to apply this theory to the explanation of various properties of gases, and to show that, besides accounting for the relations of pressure, density, and temperature in a single gas, it affords a mechanical explanation of the known chemical relation between the density of a gas and its equivalent weight, commonly called the Law of Equivalent Volumes. It also explains the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases.

The opinion that the observed properties of visible bodies apparently at rest are due to the action of invisible molecules in rapid motion is to be found in LUCRETIUS. In the exposition which he gives of the theories of DEMOCRITUS as modified by EPICURUS, he describes the invisible atoms as all moving downwards with equal velocities, which, at quite uncertain times and places, suffer an imperceptible change, just enough to allow of occasional collisions taking place between the atoms. These atoms he supposes to set small bodies in motion by an action of which we may form some conception by looking at the motes in a sunbeam. The language of LUCRETIUS must of course be interpreted according to the physical ideas of his age, but we need not wonder that it suggested to LE SAGE the fundamental conception of his theory of gases, as well as his doctrine of ultramundane corpuscles.

Professor CLAUSIUS, to whom we owe the most extensive developments of the dynamical theory of gases, has given\* a list of authors who have adopted or given countenance to any theory of invisible particles in motion. Of these, DANIEL BERNOULLI, in the tenth section of his 'Hydrodynamics,' distinctly explains the pressure of air by the impact of its particles on the sides of the vessel containing it.

CLAUSIUS also mentions a book entitled "Deux Traités de Physique Mécanique, publiés par PIERRE PREVOST, comme simple Éditeur du premier et comme Auteur du second," Genève et Paris, 1818. The first memoir is by G. LE SAGE, who explains gravity by the impact of "ultramundane corpuscles" on bodies. These corpuscles also set in motion the particles of light and various æthereal media, which in their turn act on the molecules of gases and keep up their motions. His theory of impact is faulty, but his explanation of the expansive force of gases is essentially the same as in the dynamical theory as it now stands. The second memoir, by PREVOST, contains new applications of the principles of LE SAGE to gases and to light. A more extensive application of the theory of moving molecules was made by HERAPATH†. His theory of the collisions of

\* POGGENDORFF's 'Annalen,' Jan. 1862. Translated by G. C. FOSTER, B.A., Phil. Mag. June 1862.

† Mathematical Physics, &c., by JOHN HERAPATH, Esq. 2 vols. London: Whittaker & Co., and Herapath's Railway Journal Office, 1847.

perfectly hard bodies, such as he supposes the molecules to be, is faulty, inasmuch as it makes the result of impact depend on the absolute motion of the bodies, so that by experiments on such hard bodies (if we could get them) we might determine the absolute direction and velocity of the motion of the earth\*. This author, however, has applied his theory to the numerical results of experiment in many cases, and his speculations are always ingenious, and often throw much real light on the questions treated. In particular, the theory of temperature and pressure in gases and the theory of diffusion are clearly pointed out.

Dr. JOULE† has also explained the pressure of gases by the impact of their molecules, and has calculated the velocity which they must have in order to produce the pressure observed in particular gases.

It is to Professor CLAUDIUS, of Zurich, that we owe the most complete dynamical theory of gases. His other researches on the general dynamical theory of heat are well known, and his memoirs "On the kind of Motion which we call Heat," are a complete exposition of the molecular theory adopted in this paper. After reading his investigation‡ of the distance described by each molecule between successive collisions, I published some propositions§ on the motions and collisions of perfectly elastic spheres, and deduced several properties of gases, especially the law of equivalent volumes, and the nature of gaseous friction. I also gave a theory of diffusion of gases, which I now know to be erroneous, and there were several errors in my theory of the conduction of heat in gases which M. CLAUDIUS has pointed out in an elaborate memoir on that subject||.

M. O. E. MEYER¶ has also investigated the theory of internal friction on the hypothesis of hard elastic molecules.

In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules repelling one another with a force whose direction always passes very nearly through the centres of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance.

If we suppose an imaginary plane drawn through a vessel containing a great number of such molecules in motion, then a great many molecules will cross the plane in either direction. The excess of the mass of those which traverse the plane in the positive

\* Mathematical Physics, &c., p. 134.

† Some Remarks on Heat and the Constitution of Elastic Fluids, Oct. 3, 1848.

‡ Phil. Mag. Feb. 1859.

§ Illustrations of the Dynamical Theory of Gases, Phil. Mag. 1860, January and July.

|| POGGENDORFF, Jan. 1862; Phil. Mag. June 1862.

¶ Ueber die innere Reibung der Gase (POGGENDORFF, vol. cxxv. 1865).

direction over that of those which traverse it in the negative direction, gives a measure of the flow of gas through the plane in the positive direction.

If the plane be made to move with such a velocity that there is no excess of flow of molecules in one direction through it, then the velocity of the plane is the mean velocity of the gas resolved normal to the plane.

There will still be molecules moving in both directions through the plane, and carrying with them a certain amount of momentum into the portion of gas which lies on the other side of the plane.

The quantity of momentum thus communicated to the gas on the other side of the plane during a unit of time is a measure of the force exerted on this gas by the rest. This force is called the pressure of the gas.

If the velocities of the molecules moving in different directions were independent of one another, then the pressure at any point of the gas need not be the same in all directions, and the pressure between two portions of gas separated by a plane need not be perpendicular to that plane. Hence, to account for the observed equality of pressure in all directions, we must suppose some cause equalizing the motion in all directions. This we find in the deflection of the path of one particle by another when they come near one another. Since, however, this equalization of motion is not instantaneous, the pressures in all directions are perfectly equalized only in the case of a gas at rest, but when the gas is in a state of motion, the want of perfect equality in the pressures gives rise to the phenomena of viscosity or internal friction. The phenomena of viscosity in all bodies may be described, independently of hypothesis, as follows:—

A distortion or strain of some kind, which we may call  $S$ , is produced in the body by displacement. A state of stress or elastic force which we may call  $F$  is thus excited. The relation between the stress and the strain may be written  $F=ES$ , where  $E$  is the coefficient of elasticity for that particular kind of strain. In a solid body free from viscosity,  $F$  will remain  $=ES$ , and

$$\frac{dF}{dt} = E \frac{dS}{dt}.$$

If, however, the body is viscous,  $F$  will not remain constant, but will tend to disappear at a rate depending on the value of  $F$ , and on the nature of the body. If we suppose this rate proportional to  $F$ , the equation may be written

$$\frac{dF}{dt} = E \frac{dS}{dt} - \frac{F}{T},$$

which will indicate the actual phenomena in an empirical manner. For if  $S$  be constant,

$$F = ES e^{-\frac{t}{T}},$$

showing that  $F$  gradually disappears, so that if the body is left to itself it gradually loses any internal stress, and the pressures are finally distributed as in a fluid at rest.

If  $\frac{dS}{dt}$  is constant, that is, if there is a steady motion of the body which continually

increases the displacement,

$$F = ET \frac{dS}{dt} + Ce^{-\frac{t}{T}},$$

showing that  $F$  tends to a constant value depending on the rate of displacement. The quantity  $ET$ , by which the rate of displacement must be multiplied to get the force, may be called the coefficient of viscosity. It is the product of a coefficient of elasticity,  $E$ , and a time  $T$ , which may be called the "time of relaxation" of the elastic force. In mobile fluids  $T$  is a very small fraction of a second, and  $E$  is not easily determined experimentally. In viscous solids  $T$  may be several hours or days, and then  $E$  is easily measured. It is possible that in some bodies  $T$  may be a function of  $F$ , and this would account for the gradual untwisting of wires after being twisted beyond the limit of perfect elasticity. For if  $T$  diminishes as  $F$  increases, the parts of the wire furthest from the axis will yield more rapidly than the parts near the axis during the twisting process, and when the twisting force is removed, the wire will at first untwist till there is equilibrium between the stresses in the inner and outer portions. These stresses will then undergo a gradual relaxation; but since the actual value of the stress is greater in the outer layers, it will have a more rapid rate of relaxation, so that the wire will go on gradually untwisting for some hours or days, owing to the stress on the interior portions maintaining itself longer than that of the outer parts. This phenomenon was observed by WEBER in silk fibres, by KOHLRAUSCH in glass fibres, and by myself in steel wires.

In the case of a collection of moving molecules such as we suppose a gas to be, there is also a resistance to change of form, constituting what may be called the linear elasticity, or "rigidity" of the gas, but this resistance gives way and diminishes at a rate depending on the amount of the force and on the nature of the gas.

Suppose the molecules to be confined in a rectangular vessel with perfectly elastic sides, and that they have no action on one another, so that they never strike one another, or cause each other to deviate from their rectilinear paths. Then it can easily be shown that the pressures on the sides of the vessel due to the impacts of the molecules are perfectly independent of each other, so that the mass of moving molecules will behave, not like a fluid, but like an elastic solid. Now suppose the pressures at first equal in the three directions perpendicular to the sides, and let the dimensions  $a$ ,  $b$ ,  $c$  of the vessel be altered by small quantities,  $\delta a$ ,  $\delta b$ ,  $\delta c$ .

Then if the original pressure in the direction of  $a$  was  $p$ , it will become

$$p \left( 1 - 3 \frac{\delta a}{a} - \frac{\delta b}{b} - \frac{\delta c}{c} \right);$$

or if there is no change of volume,

$$\frac{\delta p}{p} = -2 \frac{\delta a}{a},$$

showing that in this case there is a "longitudinal" elasticity of form of which the coefficient is  $2p$ . The coefficient of "Rigidity" is therefore  $=p$ .

This rigidity, however, cannot be directly observed, because the molecules continually deflect each other from their rectilinear courses, and so equalize the pressure in all directions. The rate at which this equalization takes place is great, but not infinite; and therefore there remains a certain inequality of pressure which constitutes the phenomenon of viscosity.

I have found by experiment that the coefficient of viscosity in a given gas is independent of the density, and proportional to the absolute temperature, so that if  $ET$  be the viscosity,  $ET \propto \frac{p}{\rho}$ .

But  $E=p$ , therefore  $T$ , the time of relaxation, varies inversely as the density and is independent of the temperature. Hence the number of collisions producing a given deflection which take place in unit of time is independent of the temperature, that is, of the velocity of the molecules, and is proportional to the number of molecules in unit of volume. If we suppose the molecules hard elastic bodies, the number of collisions of a given kind will be proportional to the velocity, but if we suppose them centres of force, the angle of deflection will be smaller when the velocity is greater; and if the force is inversely as the fifth power of the distance, the number of deflections of a given kind will be independent of the velocity. Hence I have adopted this law in making my calculations.

The effect of the mutual action of the molecules is not only to equalize the pressure in all directions, but, when molecules of different kinds are present, to communicate motion from the one kind to the other. I formerly showed that the final result in the case of hard elastic bodies is to cause the average *vis viva* of a molecule to be the same for all the different kinds of molecules. Now the pressure due to each molecule is proportional to its *vis viva*, hence the whole pressure due to a given number of molecules in a given volume will be the same whatever the mass of the molecules, provided the molecules of different kinds are permitted freely to communicate motion to each other.

When the flow of *vis viva* from the one kind of molecules to the other is zero, the temperature is said to be the same. Hence equal volumes of different gases at equal pressures and temperatures contain equal numbers of molecules.

This result of the dynamical theory affords the explanation of the "law of equivalent volumes" in gases.

We shall see that this result is true in the case of molecules acting as centres of force. A law of the same general character is probably to be found connecting the temperatures of liquid and solid bodies with the energy possessed by their molecules, although our ignorance of the nature of the connexions between the molecules renders it difficult to enunciate the precise form of the law.

The molecules of a gas in this theory are those portions of it which move about as a single body. These molecules may be mere points, or pure centres of force endowed with inertia, or the capacity of performing work while losing velocity. They may be systems of several such centres of force, bound together by their mutual actions, and in

this case the different centres may either be separated, so as to form a group of points, or they may be actually coincident, so as to form one point.

Finally, if necessary, we may suppose them to be small solid bodies of a determinate form; but in this case we must assume a new set of forces binding the parts of these small bodies together, and so introduce a molecular theory of the second order. The doctrines that all matter is extended, and that no two portions of matter can coincide in the same place, being deductions from our experiments with bodies sensible to us, have no application to the theory of molecules.

The actual energy of a moving body consists of two parts, one due to the motion of its centre of gravity, and the other due to the motions of its parts relative to the centre of gravity. If the body is of invariable form, the motions of its parts relative to the centre of gravity consist entirely of rotation, but if the parts of the body are not rigidly connected, their motions may consist of oscillations of various kinds, as well as rotation of the whole body.

The mutual interference of the molecules in their courses will cause their energy of motion to be distributed in a certain ratio between that due to the motion of the centre of gravity and that due to the rotation, or other internal motion. If the molecules are pure centres of force, there can be no energy of rotation, and the whole energy is reduced to that of translation; but in all other cases the whole energy of the molecule may be represented by  $\frac{1}{2}Mv^2\beta$ , where  $\beta$  is the ratio of the total energy to the energy of translation. The ratio  $\beta$  will be different for every molecule, and will be different for the same molecule after every encounter with another molecule, but it will have an average value depending on the nature of the molecules, as has been shown by CLAUSIUS. The value of  $\beta$  can be determined if we know either of the specific heats of the gas, or the ratio between them.

The method of investigation which I shall adopt in the following paper, is to determine the mean values of the following functions of the velocity of all the molecules of a given kind within an element of volume:—

- ( $\alpha$ ) the mean velocity resolved parallel to each of the coordinate axes;
- ( $\beta$ ) the mean values of functions of two dimensions of these component velocities;
- ( $\gamma$ ) the mean values of functions of three dimensions of these velocities.

The rate of translation of the gas, whether by itself, or by diffusion through another gas, is given by ( $\alpha$ ), the pressure of the gas on any plane, whether normal or tangential to the plane, is given by ( $\beta$ ), and the rate of conduction of heat through the gas is given by ( $\gamma$ ).

I propose to determine the variations of these quantities, due, 1st, to the encounters of the molecules with others of the same system or of a different system; 2nd, to the action of external forces such as gravity; and 3rd, to the passage of molecules through the boundary of the element of volume.

I shall then apply these calculations to the determination of the statical cases of the final distribution of two gases under the action of gravity, the equilibrium of tempe-

perature between two gases, and the distribution of temperature in a vertical column. These results are independent of the law of force between the molecules. I shall also consider the dynamical cases of diffusion, viscosity, and conduction of heat, which involve the law of force between the molecules.

*On the Mutual Action of Two Molecules.*

Let the masses of these molecules be  $M_1$ ,  $M_2$ , and let their velocities resolved in three directions at right angles to each other be  $\xi_1$ ,  $\eta_1$ ,  $\zeta_1$  and  $\xi_2$ ,  $\eta_2$ ,  $\zeta_2$ . The components of the velocity of the centre of gravity of the two molecules will be

$$\frac{\xi_1 M_1 + \xi_2 M_2}{M_1 + M_2}, \quad \frac{\eta_1 M_1 + \eta_2 M_2}{M_1 + M_2}, \quad \frac{\zeta_1 M_1 + \zeta_2 M_2}{M_1 + M_2}.$$

The motion of the centre of gravity will not be altered by the mutual action of the molecules, of whatever nature that action may be. We may therefore take the centre of gravity as the origin of a system of coordinates moving parallel to itself with uniform velocity, and consider the alteration of the motion of each particle with reference to this point as origin.

If we regard the molecules as simple centres of force, then each molecule will describe a plane curve about this centre of gravity, and the two curves will be similar to each other and symmetrical with respect to the line of apses. If the molecules move with sufficient velocity to carry them out of the sphere of their mutual action, their orbits will each have a pair of asymptotes inclined at an angle  $\frac{\pi}{2} - \theta$  to the line of apses. The asymptotes of the orbit of  $M_1$  will be at a distance  $b_1$  from the centre of gravity, and those of  $M_2$  at a distance  $b_2$ , where

$$M_1 b_1 = M_2 b_2.$$

The distance between two parallel asymptotes, one in each orbit, will be

$$b = b_1 + b_2.$$

If, while the two molecules are still beyond each other's action, we draw a straight line through  $M_1$  in the direction of the relative velocity of  $M_1$  to  $M_2$ , and draw from  $M_2$  a perpendicular to this line, the length of this perpendicular will be  $b$ , and the plane including  $b$  and the direction of relative motion will be the plane of the orbits about the centre of gravity.

When, after their mutual action and deflection, the molecules have again reached a distance such that there is no sensible action between them, each will be moving with the same velocity relative to the centre of gravity that it had before the mutual action, but the direction of this relative velocity will be turned through an angle  $2\theta$  in the plane of the orbit.

The angle  $\theta$  is a function of the relative velocity of the molecules and of  $b$ , the form of the function depending on the nature of the action between the molecules.

If we suppose the molecules to be bodies, or systems of bodies, capable of rotation,



internal vibration, or any form of energy other than simple motion of translation, these results will be modified. The value of  $\theta$  and the final velocities of the molecules will depend on the amount of internal energy in each molecule before the encounter, and on the particular form of that energy at every instant during the mutual action. We have no means of determining such intricate actions in the present state of our knowledge of molecules, so that we must content ourselves with the assumption that the value of  $\theta$  is, on an average, the same as for pure centres of force, and that the final velocities differ from the initial velocities only by quantities which may in each collision be neglected, although in a great many encounters the energy of translation and the internal energy of the molecules arrive, by repeated small exchanges, at a final ratio, which we shall suppose to be that of 1 to  $\beta-1$ .

We may now determine the final velocity of  $M_1$  after it has passed beyond the sphere of mutual action between itself and  $M_2$ .

Let  $V$  be the velocity of  $M_1$  relative to  $M_2$ , then the components of  $V$  are

$$\xi_1 - \xi_2, \quad \eta_1 - \eta_2, \quad \zeta_1 - \zeta_2.$$

The plane of the orbit is that containing  $V$  and  $b$ . Let this plane be inclined  $\phi$  to a plane containing  $V$  and parallel to the axis of  $x$ ; then, since the direction of  $V$  is turned round an angle  $2\theta$  in the plane of the orbit, while its magnitude remains the same, we may find the value of  $\xi_1$  after the encounter. Calling it  $\xi'_1$ ,

$$\xi'_1 = \xi_1 + \frac{M_2}{M_1 + M_2} \{ (\xi_2 - \xi_1) 2 \sin^2 \theta + \sqrt{(\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2} \sin 2\theta \cos \phi \}. \quad \dots \quad (1)$$

There will be similar expressions for the components of the final velocity of  $M_1$  in the other coordinate directions.

If we know the initial positions and velocities of  $M_1$  and  $M_2$  we can determine  $V$ , the velocity of  $M_1$  relative to  $M_2$ ;  $b$  the shortest distance between  $M_1$  and  $M_2$  if they had continued to move with uniform velocity in straight lines; and  $\phi$  the angle which determines the plane in which  $V$  and  $b$  lie. From  $V$  and  $b$  we can determine  $\theta$ , if we know the law of force, so that the problem is solved in the case of two molecules.

When we pass from this case to that of two systems of moving molecules, we shall suppose that the time during which a molecule is beyond the action of other molecules is so great compared with the time during which it is deflected by that action, that we may neglect both the time and the distance described by the molecules during the encounter, as compared with the time and the distance described while the molecules are free from disturbing force. We may also neglect those cases in which three or more molecules are within each other's spheres of action at the same instant.

#### *On the Mutual Action of Two Systems of Moving Molecules.*

Let the number of molecules of the first kind in unit of volume be  $N_1$ , the mass of each being  $M_1$ . The velocities of these molecules will in general be different both in magnitude and direction. Let us select those molecules the components of whose velocities

lie between

$$\xi_1 \text{ and } \xi_1 + d\xi_1, \quad \eta_1 \text{ and } \eta_1 + d\eta_1, \quad \zeta_1 \text{ and } \zeta_1 + d\zeta_1,$$

and let the number of these molecules be  $dN_1$ . The velocities of these molecules will be very nearly equal and parallel.

On account of the mutual actions of the molecules, the number of molecules which at a given instant have velocities within given limits will be definite, so that

$$dN_1 = f_1(\xi_1, \eta_1, \zeta_1) d\xi_1 d\eta_1 d\zeta_1 \dots \dots \dots (2)$$

We shall consider the form of this function afterwards.

Let the number of molecules of the second kind in unit of volume be  $N_2$ , and let  $dN_2$  of these have velocities between  $\xi_2$  and  $\xi_2 + d\xi_2$ ,  $\eta_2$  and  $d\eta_2 + \eta_2$ ,  $\zeta_2$  and  $\zeta_2 + d\zeta_2$ , where

$$dN_2 = f_2(\xi_2, \eta_2, \zeta_2) d\xi_2 d\eta_2 d\zeta_2.$$

The velocity of any of the  $dN_1$  molecules of the first system relative to the  $dN_2$  molecules of the second system is  $V$ , and each molecule  $M_1$  will in the time  $\delta t$  describe a relative path  $V\delta t$  among the molecules of the second system. Conceive a space bounded by the following surfaces. Let two cylindrical surfaces have the common axis  $V\delta t$  and radii  $b$  and  $b + db$ . Let two planes be drawn through the extremities of the line  $V\delta t$  perpendicular to it. Finally, let two planes be drawn through  $V\delta t$  making angles  $\phi$  and  $\phi + d\phi$  with a plane through  $V$  parallel to the axis of  $x$ . Then the volume included between the four planes and the two cylindric surfaces will be  $Vbdbd\phi\delta t$ .

If this volume includes one of the molecules  $M_2$ , then during the time  $\delta t$  there will be an encounter between  $M_1$  and  $M_2$ , in which  $b$  is between  $b$  and  $b + db$ , and  $\phi$  between  $\phi$  and  $\phi + d\phi$ .

Since there are  $dN_1$  molecules similar to  $M_1$  and  $dN_2$  similar to  $M_2$  in unit of volume, the whole number of encounters of the given kind between the two systems will be

$$Vbdbd\phi\delta t dN_1 dN_2.$$

Now let  $Q$  be any property of the molecule  $M_1$ , such as its velocity in a given direction, the square or cube of that velocity or any other property of the molecule which is altered in a known manner by an encounter of the given kind, so that  $Q$  becomes  $Q'$  after the encounter, then during the time  $\delta t$  a certain number of the molecules of the first kind have  $Q$  changed to  $Q'$ , while the remainder retain the original value of  $Q$ , so that

$$\delta Q dN_1 = (Q' - Q) Vbdbd\phi\delta t dN_1 dN_2,$$

or

$$\frac{\delta Q dN_1}{\delta t} = (Q' - Q) Vbdbd\phi dN_1 dN_2 \dots \dots \dots (3)$$

Here  $\frac{\delta Q dN_1}{\delta t}$  refers to the alteration in the sum of the values of  $Q$  for the  $dN_1$  molecules, due to their encounters of the given kind with the  $dN_2$  molecules of the second sort. In order to determine the value of  $\frac{\delta Q dN_1}{\delta t}$ , the rate of alteration of  $Q$  among all the molecules of the first kind, we must perform the following integrations:—

1st, with respect to  $\varphi$  from  $\varphi=0$  to  $\varphi=2\pi$ .

2nd, with respect to  $b$  from  $b=0$  to  $b=\infty$ . These operations will give the results of the encounters of every kind between the  $dN_1$  and  $dN_2$  molecules.

3rd, with respect to  $dN_2$ , or  $f_2(\xi_2\eta_2\zeta_2)d\xi_2d\eta_2d\zeta_2$ .

4th, with respect to  $dN_1$ , or  $f_1(\xi_1\eta_1\zeta_1)d\xi_1d\eta_1d\zeta_1$ .

These operations require in general a knowledge of the forms of  $f_1$  and  $f_2$ .

1st. *Integration with respect to  $\varphi$ .*

Since the action between the molecules is the same in whatever plane it takes place, we shall first determine the value of  $\int_0^{2\pi} (Q'-Q)d\varphi$  in several cases, making  $Q$  some function of  $\xi$ ,  $\eta$ , and  $\zeta$ .

( $\alpha$ ) Let  $Q=\xi_1$  and  $Q'=\xi'_1$ , then

$$\int_0^{2\pi} (\xi'_1 - \xi_1)d\varphi = \frac{M_2}{M_1 + M_2} (\xi_2 - \xi_1) 4\pi \sin^2 \theta. \quad \dots \dots \dots (4)$$

( $\beta$ ) Let  $Q=\xi_1^2$  and  $Q'=\xi_1'^2$ ,

$$\int_0^{2\pi} (\xi_1'^2 - \xi_1^2)d\varphi = \frac{M_2}{(M_1 + M_2)^2} \{ (\xi_2 - \xi_1)(M_1\xi_1 + M_2\xi_2) 8\pi \sin^2 \theta + M_2((\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2 - 2(\xi_2 - \xi_1)^2) \pi \sin^2 2\theta \}. \quad (5)$$

By transformation of coordinates we may derive from this

$$\int_0^{2\pi} (\xi_1'\eta_1 - \xi_1\eta_1)d\varphi = \frac{M_2}{(M_1 + M_2)^2} \{ (M_2\xi_2\eta_2 - M_1\xi_1\eta_1 + \frac{1}{2}(M_1 - M_2)(\xi_1\eta_2 + \xi_2\eta_1)) 8\pi \sin^2 \theta - 3M_2(\xi_2 - \xi_1)(\eta_2 - \eta_1) \}, \quad (6)$$

with similar expressions for the other quadratic functions of  $\xi$ ,  $\eta$ ,  $\zeta$ .

( $\gamma$ ) Let  $Q=\xi_1(\xi_1^2 + \eta_1^2 + \zeta_1^2)$ , and  $Q'=\xi'_1(\xi_1'^2 + \eta_1'^2 + \zeta_1'^2)$ ; then putting  $\xi_1^2 + \eta_1^2 + \zeta_1^2 = V_1^2$ ,  $\xi_1\xi_2 + \eta_1\eta_2 + \zeta_1\zeta_2 = U$ ,  $\xi_2^2 + \eta_2^2 + \zeta_2^2 = V_2^2$ , and  $(\xi_2 - \xi_1)^2 + (\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2 = V^2$ , we find

$$\int_0^{2\pi} (\xi_1'V_1'^2 - \xi_1V_1^2)d\varphi = \left. \begin{aligned} & \frac{M_2}{M_1 + M_2} 4\pi \sin^2 \theta \{ (\xi_2 - \xi_1)V_1^2 + 2\xi_1(U - V_1^2) \\ & + \left( \frac{M_2}{M_1 + M_2} \right)^2 (8\pi \sin^2 \theta - 3\pi \sin^2 2\theta) 2(\xi_2 - \xi_1)(U - V_1^2) \\ & + \left( \frac{M_2}{M_1 + M_2} \right)^2 (8\pi \sin^2 \theta + 2\pi \sin^2 2\theta) \xi_1 V^2 \\ & + \left( \frac{M_2}{M_1 + M_2} \right)^3 (8\pi \sin^2 \theta - 2\pi \sin^2 2\theta) 2(\xi_2 - \xi_1)V^2. \end{aligned} \right\} \dots \dots (7)$$

These are the principal functions of  $\xi$ ,  $\eta$ ,  $\zeta$  whose changes we shall have to consider; we shall indicate them by the symbols  $\alpha$ ,  $\beta$ , or  $\gamma$ , according as the function of the velocity is of one, two, or three dimensions.

2nd. *Integration with respect to  $b$ .*

We have next to multiply these expressions by  $bdb$ , and to integrate with respect to  $b$  from  $b=0$  to  $b=\infty$ . We must bear in mind that  $\theta$  is a function of  $b$  and  $V$ , and can only be determined when the law of force is known. In the expressions which we have

to deal with,  $\theta$  occurs under two forms only, namely,  $\sin^2\theta$  and  $\sin^2 2\theta$ . If, therefore, we can find the values of

$$B_1 = \int_0^\infty 4\pi b db \sin^2\theta, \quad \text{and} \quad B_2 = \int_0^\infty \pi b db \sin^2 2\theta, \quad . . . . . \quad (8)$$

we can integrate all the expressions with respect to  $b$ .

$B_1$  and  $B_2$  will be functions of  $V$  only, the form of which we can determine only in particular cases, after we have found  $\theta$  as a function of  $b$  and  $V$ .

*Determination of  $\theta$  for certain laws of Force.*

Let us assume that the force between the molecules  $M_1$  and  $M_2$  is repulsive and varies inversely as the  $n$ th power of the distance between them, the value of the moving force at distance unity being  $K$ , then we find by the equation of central orbits,

$$\frac{\pi}{2} - \theta = \int_0^{x'} \frac{dx}{\sqrt{1 - x^2 - \frac{2}{n-1} \left(\frac{x}{\alpha}\right)^{n-1}}}, \quad . . . . . \quad (9)$$

where  $x = \frac{b}{r}$ , or the ratio of  $b$  to the distance of the molecules at a given time:  $x$  is therefore a numerical quantity;  $\alpha$  is also a numerical quantity and is given by the equation

$$\alpha = b \left( \frac{V^2 M_1 M_2}{K(M_1 + M_2)} \right)^{\frac{1}{n-1}} . . . . . \quad (10)$$

The limits of integration are  $x=0$  and  $x=x'$ , where  $x'$  is the least positive root of the equation

$$1 - x^2 - \frac{2}{n-1} \left(\frac{x}{\alpha}\right)^{n-1} = 0. \quad . . . . . \quad (11)$$

It is evident that  $\theta$  is a function of  $\alpha$  and  $n$ , and when  $n$  is known  $\theta$  may be expressed as a function of  $\alpha$  only.

Also

$$b db = \left( \frac{K(M_1 + M_2)}{V^2 M_1 M_2} \right)^{\frac{2}{n-1}} \alpha d\alpha; \quad . . . . . \quad (12)$$

so that if we put

$$A_1 = \int_0^\infty 4\pi \alpha d\alpha \sin^2\theta, \quad A_2 = \int_0^\infty \pi \alpha d\alpha \sin^2 2\theta, \quad . . . . . \quad (13)$$

$A_1$  and  $A_2$  will be definite numerical quantities which may be ascertained when  $n$  is given,

and  $B_1$  and  $B_2$  may be found by multiplying  $A_1$  and  $A_2$  by  $\left( \frac{K(M_1 + M_2)}{M_1 M_2} \right)^{\frac{2}{n-1}} V^{\frac{-4}{n-1}}$ .

Before integrating further we have to multiply by  $V$ , so that the form in which  $V$  will enter into the expressions which have to be integrated with respect to  $dN_1$  and  $dN_2$  will be

$$V^{\frac{n-5}{n-1}}$$

It will be shown that we have reason from experiments on the viscosity of gases to believe that  $n=5$ . In this case  $V$  will disappear from the expressions of the form (3), and they will be capable of immediate integration with respect to  $dN_1$  and  $dN_2$ .