On the Stationary Motion of a System of Equal Elastic Spheres of Finite Diameter. By S. H. BURBURY, M.A., F.R.S. Read December 10th, 1896. Received in revised form May 15th, 1897.

1. The object of this paper is to prove that in such a system in stationary motion the velocities of spheres near to one another are *correlated*. That is, that the chance that n spheres forming a group together in space shall simultaneously have component velocities

$$u_1 \dots u_1 + du_1, \quad v_1 \dots v_1 + dv_1, \quad \dots \quad w_n \dots w_n + dw_n$$

is of the form

$$Ae^{-\lambda Q} du_1 \dots dw_n,$$

and Q is not merely the sum of the squares, as in Maxwell's system, but a quadratic function, of the velocities, namely,

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

the second term containing the products of every pair of u 's, &c., but no products uv , uw , or vw , and b being a function of the distance at the instant between the two molecules whose velocities are u , &c., and u' , &c., which becomes evanescent as that distance increases.

The sufficiency of Maxwell's distribution of velocities, according to which Q contains only the squares of the velocities, has been proved by several writers, but always on a certain fundamental assumption, which is true only for infinitely small densities—The assumption is in effect this—let $f dx dy dz du dv dw$ be the number per unit volume of molecules whose coordinates of position, x , y , z , and momenta u , v , w , are in a certain state A , or, as we may express it, $f dx \dots dw$ is the chance that a molecule shall be in that state. Similarly, $f' dx' \dots dw'$ is the chance that another molecule shall be in the state A' . Then it is always assumed that the chance of two molecules being in the states A , A' respectively is $ff' du \dots dw'$. That is, it is assumed that the chances are under all circumstances, *i.e.*, even when the two molecules are on the point of collision, independent.*

* See especially Boltzmann's *Vorlesungen über Gas Theorie*, 1895, p. 22, where the assumption is made emphatically.

That assumption involves the non-existence of my coefficient b .

It will be sufficient for my present purpose to prove the necessity of the b term when the molecules are elastic spheres of finite diameter. For, if that be proved, it will be admitted that it must exist in more general cases.

Art. 15, Equations (I.) and (24), (25) show the line of argument.

I claim as an advantage of the formula that it gives a limit of density, or density and temperature, beyond which the formula cannot hold, and the motion must change type. The ordinary formula, in which Q contains squares only, is either true only in the limiting case of infinitely small density—i.e., when the aggregate volume of all the spheres in unit volume is infinitely small—or it is true however great the density. There is no intermediate point at which we can with reason draw the line. Using my formula, we have such a point. For, as the density increases, b increases, until the determinant of Q , namely,

$$D = \begin{vmatrix} 2 & b_{12} & b_{13} & 1 \\ b_{12} & 2 & . & . \\ . & . & . & . \end{vmatrix}$$

or some one of its coaxial minors becomes zero, or negative. And then Q will for some values of the u 's, v 's and w 's become negative. And the law necessarily fails. The change of type of the system's motion is represented mathematically by the vanishing of the determinant.

2. It is necessary first to treat the case where the molecules are of infinitely small dimensions, so that collisions between them will not occur. That being the case, the system will be in stationary motion if the velocities are distributed according to Maxwell's law, Q being a sum of squares only. This we may admit, whatever views we may hold as to the possibility of a distribution according to any other law. I shall then assume that distribution to exist. And it follows, from Q being a sum of squares only, that the fact of any molecule, or any group of molecules, having any given velocities affords (if the whole number of molecules considered be infinite) no presumption whatever with regard to the velocities of any other molecules.

3. Let ρ be the average number of molecules in unit of volume, the system being homogeneous in this respect. We may suppose the whole system to be comprised within an elastic boundary at an infinite distance which reverses the velocities of all molecules which strike it, so that ρ may be regarded as invariable with the time.

4. Let P be any point, r the distance of any other point from P . Let f be a function of r which satisfies the following conditions, namely,

(A) f is equal to unity at all points within a small sphere of radius a described about P as centre.

(B) f is finite positive and continuous everywhere.

(C) f is of negative degree at all points outside of the a sphere.

We may take for a the radius of a sphere which on average contains one molecule.

5. Let $\alpha_1\beta_1\gamma_1, \alpha_2\beta_2\gamma_2, \dots, \alpha_n\beta_n\gamma_n$ be the component velocities in x, y , and z of the n molecules which at any instant are contained within a sphere of very great radius R described about P as centre. And let

$$\xi = \frac{\sum \alpha f}{\sum f}, \quad \eta = \frac{\sum \beta f}{\sum f}, \quad \zeta = \frac{\sum \gamma f}{\sum f}, \quad (1)$$

the summation including all the n molecules, and f having for each molecule the value proper to its position, as f_1 for the molecule whose velocities are $\alpha_1, \beta_1, \gamma_1$, &c. ξ, η, ζ are then, R being very great, continuous functions of x, y , and z .

6. Now the chance that the n molecules shall at any instant have, for their component velocities in $x, \alpha_1 \dots \alpha_1 + d\alpha_1$, &c., is

$$Ae^{-h^2u} d\alpha_1 \dots d\alpha_n,$$

and in the system now under consideration

$$Q = \alpha_1^2 + \alpha_2^2 + \dots + \alpha_n^2.$$

But, from (1), $\alpha_n f_n = \xi \sum f - \alpha_1 f_1 - \dots - \alpha_{n-1} f_{n-1}$.

Further, we may suppose the molecule to which the suffix n belongs to be very near P , whence, from condition (A) of Art. 4,

$$f_n = 1,$$

and

$$\alpha_n = \xi \sum f - \alpha_1 f_1 - \dots - \alpha_{n-1} f_{n-1}.$$

Substituting this value for a_n in Q , we obtain

$$\left. \begin{aligned} Q &= \xi^2 (\Sigma f)^2 + (1+f_1^2) a_1^2 + (1+f_2^2) a_2^2 + \&c. \\ &- 2f_1 a_1 \xi \Sigma f - 2f_2 a_2 \xi \Sigma f - \&c. \\ &+ 2f_1 f_2 a_1 a_2 + 2f_1 f_3 a_1 a_3 + 2f_2 f_3 a_2 a_3 + \&c. \end{aligned} \right\} \quad (2)$$

7. If we now integrate e^{-hQ} for $a_1, a_2, a_3, \dots a_{n-1}$ successively between limits $\pm\infty$, we get the result next stated. Let D be the determinant of Q , that is,

$$D = \begin{vmatrix} 2(\Sigma f)^2 & -2f_1 \Sigma f & -2f_2 \Sigma f & \dots \\ -2f_1 \Sigma f & (2+2f_1^2) & 2f_1 f_2 & \dots \\ -2f_2 \Sigma f & 2f_1 f_2 & (2+2f_2^2) & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

in which every constituent contains the factor 2. And let D_{pq} be the minor formed by omitting the p^{th} row and q^{th} column. Similarly, let D_{pqrs} be the minor formed by omitting rows p and r and columns q and s .

Then, by integrating for $a_1 \dots a_{n-1}$, Q is reduced to

$$\frac{D}{D_{11}},$$

$$\text{whence} \quad \xi^2 = \frac{D_{11}}{hD}. \quad (3)$$

Also by integrating for $a_2 \dots a_{n-1}$ only, we reduce Q to

$$Q' = \frac{1}{2} \frac{D_{11}}{D_{1221}} a_1^2 + \frac{D_{12}}{D_{1221}} a_1 \xi + \frac{1}{2} \frac{D_{22}}{D_{1221}} \xi^2.$$

8. Again, we find

$$\left. \begin{aligned} D_{11} &= 2^{n-1} (1+f_1^2 + \dots + f_{n-1}^2) \\ &= 2^{n-1} \Sigma f^2, \quad \text{since } f_n^2 = 1, \\ D_{1221} &= 2^{n-2} (\Sigma f^2 - f_1^2), \\ D_{1123} &= 2^{n-2} f_1 f_2, \\ D_{22} &= 2^{n-1} (\Sigma f)^2, \\ D_{12} &= -2^{n-1} f_1 \Sigma f. \end{aligned} \right\} \quad (4)$$

9. We have then for the chance that a_1 and ξ shall lie within assigned limits, whatever $a_2 \dots a_{n-1}$ may be, the expression

$$Ae^{-\lambda a'} da_1 d\xi,$$

and
$$Q' = \frac{\Sigma f^2}{\Sigma f^2 - f_1^2} a_1^2 - 2 \frac{f_1 \Sigma f}{\Sigma f^2 - f_1^2} a_1 \xi + \frac{(\Sigma f)^2}{\Sigma f^2 - f_1^2} \xi^2,$$

Let us write a for a_1 . Then, if for brevity we put

$$\frac{\Sigma f}{\Sigma f^2 - f_1^2} = q, \quad \text{and} \quad f_1 = 1,$$

$$Q' = a^2 - 2qa\xi + q\Sigma f\xi^2.$$

10. Now, if at $P \xi = 0$, and at P' , near P , $\xi = \partial\xi$, the chance that at P' a shall lie within assigned limits is $Ae^{-\lambda a'} (1 + 2ha\partial\xi)$. But, if at $P \xi \neq 0$, let us use, instead of a, β, γ ,

$$u = a - \xi, \quad v = \beta - \eta, \quad w = \gamma - \zeta,$$

or
$$a = u + \xi, \quad \beta = v + \eta, \quad \gamma = w + \zeta,$$

and
$$\begin{aligned} Q' &= (u + \xi)^2 - 2q(u + \xi)\xi + q\Sigma f\xi^2 \\ &= u^2 + 2(1 - q)\xi u + (1 - 2q + q\Sigma f)\xi^2 \\ &= \phi(u, \xi), \text{ suppose.} \end{aligned}$$

If ξ be the value of that function at P , $\xi + \partial\xi$ its value at P' , and if $\phi_1(u, \xi)$ be the value of $\phi(u, \xi)$ at P' , then

$$\phi_1(u, \xi) - \phi(u, \xi) = \partial\xi \frac{d}{d\xi} \phi(u, \xi).$$

Again, let $\phi(u) du$ be the chance that at P u shall have the value $u \dots u + du$, whatever ξ may be, that is,

$$\phi(u) = \int_{-\infty}^{\infty} d\xi \phi(u, \xi),$$

and the same chance at P' , or $\phi_1(u)$ is

$$\phi_1(u) = \int_{-\infty}^{\infty} d\xi \phi(u, \xi) + \partial\xi \int_{-\infty}^{\infty} d\xi \frac{d}{d\xi} \phi(u, \xi).$$

11. Also
$$\frac{\partial}{\partial \xi} \phi(u, \xi) = \left(\frac{d}{d\xi} \right) \phi(u, \xi) - \frac{\partial}{\partial u} \phi(u, \xi),$$

if $\left(\frac{d}{d\xi} \right)$ denotes differentiation with u constant. So

$$\phi_1(u) - \phi(u) = \partial \xi \int_{-\infty}^{\infty} d\xi \left(\frac{d}{d\xi} \right) \phi(u, \xi) - \partial \xi \int_{-\infty}^{\infty} d\xi \frac{\partial}{\partial u} \phi(u, \xi).$$

But
$$\int_{-\infty}^{\infty} d\xi \left(\frac{d}{d\xi} \right) \phi(u, \xi) = 0,$$

because $\phi(u, \xi)$ vanishes at either limit.

Therefore

$$\begin{aligned} \phi_1(u) - \phi(u) &= -\partial \xi \int_{-\infty}^{\infty} d\xi \frac{\partial}{\partial u} \phi(u, \xi) \\ &= \partial \xi \int_{-\infty}^{\infty} d\xi \phi(u, \xi) [2hu + 2h(1-q)\xi], \end{aligned}$$

and this is proportional to

$$e^{-h'u} 2h'u \partial \xi, \quad (5)$$

with h' nearly equal to h .

12. Let us now conceive the whole space in which our molecules are moving to be divided into cubes whose edges are parallel to the coordinate axes respectively, and of length $2a$. We may suppose $\frac{d\xi}{dz} + \frac{d\xi}{dx}$ to be the mean value of that function throughout any such cube. Let $\overline{uv}$ be the mean value of uv for all the molecules which at any instant are within any such cube S . Let

$$M = \Sigma \overline{uv} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right), \quad (6)$$

the summation being for all such cubes. (See p. 340, Note.)

There are two other functions symmetrical with M , namely,

$$\Sigma \overline{uv} \left(\frac{d\xi}{dy} + \frac{d\eta}{dx} \right), \quad \text{and} \quad \Sigma \overline{vw} \left(\frac{d\eta}{dz} + \frac{d\xi}{dy} \right).$$

It is sufficient to deal with M .

13. In stationary motion M is invariable with the time, or

$$\frac{dM}{dt} = 0 = \Sigma \overline{uw} \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) + \Sigma \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \frac{d}{dt} \overline{uw}. \quad (7)$$

And $\overline{uw}$ now varies with the time for the cubical spaces under consideration by the passage of molecules into or out of them. That is, generally,

$$\frac{d}{dt} \overline{uw} \neq 0.$$

We proceed to prove that in the medium of material points $\frac{d}{dt} \overline{uw}$ is of the opposite sign to, and proportional to, $\frac{d\xi}{dz} + \frac{d\zeta}{dx}$, so that the second term in $\frac{dM}{dt}$ consists of terms of the form

$$-E \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)^2,$$

where E is a positive constant.

14. Consider the cubical space S bounded by the planes

$$x = a, \quad x = -a,$$

$$y = a, \quad y = -a,$$

$$z = a, \quad z = -a.$$

The origin is then at the centre of S . Now during the short time dt $\overline{uw}$ is not on average affected by the motion of any molecules which during the whole of that time remain within S , because, there being no collisions, α, β, γ remain unchanged with the time for every individual molecule, and ξ is as likely to be increased as diminished. The function $\overline{uw}$ can vary during dt only by the passage of molecules out of and into S .

Further, under the circumstances supposed, ξ varying only in z , and ζ only in x , $\overline{uw}$ cannot vary on average by the passage of molecules out of or into S , through the faces parallel to xz , but only through the faces parallel to xy and yz .

Let ξ be the value of that function at the centre of S . Then, a being small, the value on the plane $z = a$ is $\xi + a \frac{d\xi}{dz}$. Similarly, on the plane $x = a$, ζ becomes $\zeta + a \frac{d\zeta}{dx}$. And on the plane $z = a$, given that ξ has the above value, the number per unit of volume of molecules for which u, v, w lie within the limits $u \dots u + du$, &c., that is, the

number of the class $(u v w)$ is, by Art. 11,

$$\rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(1 + 2hua \frac{dz}{dz}\right), \text{ by (5),}$$

where A is a known constant, and h is written for h' of Art. 11.

If γ be negative, they enter the space S , if γ be positive, they pass out of the space S , at a rate per unit of area and time

$$\rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(1 + 2hua \frac{dz}{dz}\right) \gamma,$$

that is, on average

$$\rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(1 + 2hua \frac{dz}{dz}\right) w,$$

and the rate of entry or exit for the whole face of cube S on the plane $z = a$ is

$$4a^3 \rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(1 + 2hua \frac{dz}{dz}\right) w.$$

Therefore the class $(u v w)$ is increased in number per unit of time by the passage of molecules through the plane $z = a$ by the quantity

$$-4a^3 \rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(w + 2huwa \frac{dz}{dz}\right).$$

For the plane $z = -a$, we change the sign of a and w , molecules now entering S with positive w , and the corresponding expression is

$$4a^3 \rho A e^{-h(u^2+v^2+w^2)} du dv dw \left(w - 2huwa \frac{dz}{dz}\right).$$

For both faces the increase in number of the same class per unit of time is

$$-8a^3 \rho A e^{-h(u^2+v^2+w^2)} du dv dw \cdot 2huwa \frac{dz}{dz}.$$

By symmetry between x and z the same class is increased in number per unit of time by the passage of molecules through the faces $x = a$ and $x = -a$, by

$$-8a^3 \rho A e^{-h(u^2+v^2+w^2)} du dv dw \cdot 2huwa \frac{dz}{dx}.$$

If therefore $f(u v w) du dv dw$ be the number of the class $(u v w)$ within S ,

$$\frac{d}{dt} f(u v w) = -8a^3 \rho A e^{-h(u^2+v^2+w^2)} 2huwa \left(\frac{dz}{dz} + \frac{dz}{dx}\right). \quad (8)$$

But
$$\overline{uw} = \iiint_{-\infty}^{\infty} uw f(u v w) du dv dw \div 8a^3 p;$$

and therefore

$$\begin{aligned} \frac{d}{dt} \overline{uw} &= \iiint_{-\infty}^{\infty} uw \frac{d}{dt} f(u v w) du dv dw \div 8a^3 p \\ &= -A \iiint_{-\infty}^{\infty} e^{-h(u^2+v^2+w^2)} u^2 w^2 du dv dw \cdot 2h \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \\ &= -\frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right); \end{aligned}$$

and therefore

$$\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \frac{d}{dt} \overline{uw} = -\frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)^2. \quad (9)$$

It will be observed that $\frac{d}{dt}(\overline{uw})$, thus considered, is proportional to the rate $(-w)$ at which positive momentum, denoted by u , is transferred across the plane $z = a$, in direction of negative z , or at which positive momentum in direction z is transferred across the plane $x = a$, in direction of negative x . So that, if by any change in the nature of the molecule that rate of transfer were increased, $\frac{d}{dt} \overline{uw}$ would be increased in the same proportion. See *post*, Art. 16.

15. We have then in stationary motion of the system of material points

$$\begin{aligned} \frac{dM}{dt} &= 0, \\ &= \Sigma \overline{uw} \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) - \Sigma \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)^2. \end{aligned} \quad (I.)$$

It is not necessary to evaluate the first term, but it is important for the purposes of Art. 23, *post*, to observe its form. The function $\frac{d\xi}{dz} \partial z$ at P is the difference between the value of ξ at P and its value at a point distant ∂z from P in direction z . Therefore

$$\begin{aligned} \Sigma_f \frac{d\xi}{dz} &= -\Sigma_a \frac{df}{dz} \\ &= -\Sigma_a \frac{z}{r} \frac{df}{dr}, \end{aligned}$$

Consider a molecule with component velocities α, β, γ , and about it a sphere of radius r (a little greater than a of Art. 4). Let xyz and xyz' be two points on that sphere, and $z' = -z$. Let ξ, f relate to xyz , and ξ', f' to xyz' . Then, integrating throughout the sphere, we have

$$\iiint dx dy dz \frac{d\xi}{dz} = \iint dx dy (\xi - \xi'),$$

and if $\frac{d}{dt}$ denote the change due to the motion of the molecule, and Ω be the volume of the sphere,

$$\Omega \frac{d}{dt} \frac{d\xi}{dz} = -\frac{1}{\Sigma f} \iint dx dy \left(\alpha \frac{d}{dx} + \beta \frac{d}{dy} + \gamma \frac{d}{dz} \right) \alpha (f - f'),$$

whence

$$\begin{aligned} uw \frac{d}{dt} \frac{d\xi}{dz} &= -uw\alpha\gamma \frac{1}{\Sigma f} \frac{1}{r} \frac{df}{dr} \\ &= -u^3w^3 \frac{1}{\Sigma f} \frac{1}{r} \frac{df}{dr} \end{aligned}$$

on average, and

$$\overline{uw} \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\xi'}{dz} \right) = -2\overline{u^3w^3} \frac{1}{\Sigma f} \frac{1}{r} \frac{df}{dr}. * \quad (9a)$$

It will be observed that $\frac{d}{dt} \frac{d\xi}{dz}$ thus considered is proportional to the rate (w) at which positive momentum, denoted by u , is transferred across any plane parallel to xy in direction z . And therefore, if by any change in the condition of the molecules that rate of transfer were increased, $\frac{d}{dt} \frac{d\xi}{dz}$, and similarly $\frac{d}{dt} \frac{d\xi'}{dz}$, would be increased in the same proportion. See Art. 16, *post*.

* It may be objected that the method of Arts. 14 and 15 is only applicable to a space containing many molecules, whereas our cube S is very small. But we may, in Art. 14, consider an infinite number of such cubes for all of which $\left(\frac{d\xi}{dz} + \frac{d\xi'}{dz} \right)$ has at the instant the same mean value. The method is then applicable to the sum of such spaces, and to each space on average.

16. We now pass to the case in which our molecules, instead of being material points, are elastic spheres, each of unit mass and diameter c . One known effect of this is that the quantity of momentum transferred across any plane per unit of area and time is increased in a certain ratio, $1 : 1 + \kappa$, where, in the case of elastic spheres, $\kappa = \frac{2}{3}\pi c^3\rho$. This increases both terms in (I.) in the same ratio, and therefore, so far as this property is concerned, $\frac{dM}{dt}$ remains zero. This effect arises from the usual convention concerning elastic bodies, according to which there is on every collision an instantaneous transfer of momentum through a certain space. It has nothing to do with the change of direction of the relative velocity, which also occurs on collision, and which we shall have to consider. The first effect would take place in precisely the same way, if after every collision the direction of the relative velocity were restored by Maxwell's corps of demons to what it was before collision.

17. Since every collision changes the direction of motion of the colliding spheres, the expression in Art. 14 derived from

$$\left(\frac{d\xi}{dz} + \frac{d\xi}{dx}\right) \frac{d\overline{uv}}{dt}$$

contains, in addition to the result calculated in that article, a new term derived from collisions which we have now to calculate.

Let V be the half relative velocity of two molecules, λ, μ, ν its direction cosines before collision, λ', μ', ν' after collision. Let $\lambda V = V_x$, $\nu V = V_z$. The number of collisions per unit of volume and time for given V is $2\pi c^3\rho V$. Hence, for the change with the time of $V_x V_z$ due to collisions with given V , we have

$$2\pi c^3\rho V \cdot V^2 (\overline{\lambda'\nu'} - \overline{\lambda\nu}),$$

the bar denoting mean values. We have now to find the values of $\overline{\lambda'\nu'}$ and $\overline{\lambda\nu}$ for all collisions, given V .

At the instant of collision let the centres of the two colliding molecules be A, B ; so that AB is the line of centres. Let BD be the relative velocity. Or, if $DE = BE$, one molecule has velocity DE , and the other BE , in addition to the velocity of their common centre of inertia, whatever that may be. Let the angle $DBA = \theta$. If $AO = BO$, O is the point of contact.

Let BX, BZ be the directions of the axes of x and z , and let the

angle between the planes DBA and DBZ be ϕ , and the angle between the planes DBA and DBX be ϕ' .

Then, if x_0, z_0 be the x and z coordinates of A referred to O as origin, and if the direction BE be that of $\lambda\mu\nu$,

$$\left. \begin{aligned} z_0 &= -\nu \frac{c}{2} \cos \theta + \frac{c}{2} \sqrt{1-\nu^2} \sin \theta \cos \phi, \\ x_0 &= -\lambda \frac{c}{2} \cos \theta + \frac{c}{2} \sqrt{1-\lambda^2} \sin \theta \cos \phi'. \end{aligned} \right\} \quad (10)$$

The complete definition of ϕ shall be this:—

When the plane DBA , turning round DB , contains the axis of z , $\phi = 0$ for that position of BA which makes the least angle with the axis of positive z . And ϕ' has a corresponding definition for the axis of x (see 20, *post*).

18. If ξ_0, ζ_0 be the values of ξ and ζ at O , then at A

$$\left. \begin{aligned} \xi - \xi_0 &= \frac{c}{2} (-\nu \cos \theta + \sqrt{1-\nu^2} \sin \theta \cos \phi) \frac{d\xi}{dz}, \\ \zeta - \zeta_0 &= \frac{c}{2} (-\lambda \cos \theta + \sqrt{1-\lambda^2} \sin \theta \cos \phi') \frac{d\zeta}{dx}. \end{aligned} \right\} \quad (11)$$

Then, by the same reasoning as in Art. 11, the number per unit of volume of pairs of molecules whose components of half relative velocity are $V_x \dots V_x + dV_x, V_y \dots V_y + dV_y$, and $V_z \dots V_z + dV_z$ is at A

$$C e^{-2h(V_x^2 + V_y^2 + V_z^2)} dV_x dV_y dV_z \{1 + 2h\lambda V \xi - \xi_0 + 2h\nu V \zeta - \zeta_0\},$$

where C is the usual constant for this case. Hence we find, for the

mean value of $V_x V_x$ for all collisions, given V ,

$$\overline{V_x V_x} = C e^{-2hV^2} V^2 dV_x dV_y dV_z \lambda \nu \\ \times \int_0^{1\pi} 2 \sin \theta \cos \theta d\theta \int_0^\pi d\phi \{1 + 2h\lambda V \overline{\xi - \xi_0} + 2h\nu V \overline{\zeta - \zeta_0}\},$$

divided by $C e^{-2hV^2} V^2 dV_x dV_y dV_z$,

and the general mean values of functions of λ, μ, ν being taken after integration according to θ and ϕ .

That is,

$$\begin{aligned} \overline{V_x V_x} &= V^2 \overline{\lambda \nu} \int_0^{1\pi} d\theta \, 2 \sin \theta \cos \theta \\ &\quad + V^2 \frac{d\overline{\xi}}{dz} \int_0^{1\pi} d\theta \int_0^\pi d\phi \, 2 \sin \theta \cos \theta \, 2h\lambda^2 \nu \frac{c}{2} (-\nu \cos \theta + \sqrt{1-\nu^2} \sin \theta \cos \phi) \\ &\quad + V^2 \frac{d\overline{\zeta}}{dx} \int_0^{1\pi} d\theta \int_0^\pi d\phi' \, 2 \sin \theta \cos \theta \, 2h\nu^2 \lambda \frac{c}{2} (-\lambda \cos \theta + \sqrt{1-\lambda^2} \sin \theta \cos \phi') \\ &= -\frac{2hc}{3} V^2 \overline{\lambda^2 \nu^2} \left(\frac{d\overline{\xi}}{dz} + \frac{d\overline{\zeta}}{dx} \right), \quad \text{because} \quad \overline{\lambda \nu} = 0 \\ &= -\frac{2hc}{3} V^2 \frac{1}{3.5} \left(\frac{d\overline{\xi}}{dz} + \frac{d\overline{\zeta}}{dx} \right), \quad \text{because} \quad \overline{\lambda^2 \nu^2} = \frac{1}{3.5}. \end{aligned} \quad (12)$$

19. We have thus proved that, on the average of all *colliding pairs* of spheres, $\overline{\lambda \nu}$ or $\overline{V_x V_x}$ is, before collision, of the opposite sign to $\left(\frac{d\overline{\xi}}{dz} + \frac{d\overline{\zeta}}{dx} \right)$. This proposition does not depend on the result of collisions. It is therefore true if, instead of elastic spheres, the molecules be centres of force, or whatever be their form.

20. We have next to calculate the mean value for all collisions of $\lambda' \nu'$, or the value of $\lambda \nu$ after collision. This will depend on the form of the molecule, and we shall now deal only with elastic spheres. It will be found that $\lambda' \nu'$ is of the same sign with $\left(\frac{d\overline{\xi}}{dz} + \frac{d\overline{\zeta}}{dx} \right)$.

We use the same notation as before. When the plane DBA turns round DB until it contains the axis of z , let A, A' , which are on opposite sides of DB , be the two positions in which that plane is cut by the

circle which A describes. Let A_x be nearer to the positive axis of x than A'_x . Then, for A_x , $\phi = 0$; for A'_x , $\phi = \pi$. Similarly, when the plane turning round DB contains the axis of x , A_x , A'_x are the two positions of A in that plane, and, if A_x be nearer than A'_x to the positive axis of x , $\phi' = 0$ for A_x , $\phi' = \pi$ for A'_x .

Let ϵ be the angle between the plane of DB and z and the plane of DB and x , so that $\phi' = \phi - \epsilon$, $\phi = \phi' + \epsilon$. It will be seen that, if $\lambda\nu$ is negative, $\cos \epsilon$ is positive; if $\lambda\nu$ is positive, $\cos \epsilon$ is negative.* In either

$$\text{case} \quad \cos \epsilon = \frac{-\lambda\nu}{\sqrt{1-\lambda^2}\sqrt{1-\nu^2}};$$

we have then, to find λ' and ν' ,

$$\left. \begin{aligned} \nu' &= -\nu \cos 2\theta + \sqrt{1-\nu^2} \sin 2\theta \cos \phi, \\ \lambda' &= -\lambda \cos 2\theta + \sqrt{1-\lambda^2} \sin 2\theta \cos \phi'; \end{aligned} \right\} \quad (13)$$

* This is most easily seen by considering the case in which V , or DB , is nearly in the plane of zx . Evidently, if $\lambda\nu$ be negative, the angle between the planes

$BD A_x$ and $BD A'_x$ is acute with the above definition of A_x and A'_x . If $\lambda\nu$ be positive, it is obtuse.

whence we derive the two symmetrical systems, namely :

$$\left. \begin{aligned} \nu' &= -\nu \cos 2\theta + \sqrt{1-\nu^2} \sin 2\theta \cos \phi, \\ \lambda' &= -\lambda \cos 2\theta - \frac{\lambda\nu}{\sqrt{1-\nu^2}} \sin 2\theta \cos \phi; \end{aligned} \right\} \quad (13a)$$

$$\text{or} \quad \left. \begin{aligned} \nu' &= -\nu \cos 2\theta - \frac{\lambda\nu}{\sqrt{1-\lambda^2}} \sin 2\theta \cos \phi', \\ \lambda' &= -\lambda \cos 2\theta + \sqrt{1-\lambda^2} \sin 2\theta \cos \phi'. \end{aligned} \right\} \quad (13b)$$

The term involving sine will disappear in the subsequent integration, and is omitted. The above systems hold for all values of λ and ν .

21. We now find that, for given V ,

$$V^2 \overline{\lambda' \nu'} = V^2 \int_0^{1^*} d\theta \int_0^\pi d\phi \, 2 \sin \theta \cos \theta (1 + 2h\lambda V \overline{\xi - \xi_0} + 2h\nu V \overline{\xi - \xi_0}) \lambda' \nu'.$$

But, with the above values of λ' , ν' ,

$$\int_0^{1^*} d\theta \int_0^\pi d\phi \, 2 \sin \theta \cos \theta \lambda' \nu' = 0,$$

as is easily seen. Therefore

$$\begin{aligned} V^2 \overline{\lambda' \nu'} &= V^2 \int_0^{1^*} d\theta \int_0^\pi d\phi \, 2 \sin \theta \cos \theta (2h\lambda V \overline{\xi - \xi_0} + 2h\nu V \overline{\xi - \xi_0}) \lambda' \nu' \\ &= 2hcV^3 \int_0^{1^*} d\theta \int_0^\pi d\phi \sin \theta \cos \theta \lambda (-\nu \cos \theta + \sqrt{1-\nu^2} \sin \theta \cos \phi) \frac{d\xi}{dz} \lambda' \nu' \\ &\quad + 2hcV^3 \int_0^{1^*} d\theta \int_0^\pi d\phi' \sin \theta \cos \theta \nu (-\lambda \cos \theta + \sqrt{1-\lambda^2} \sin \theta \cos \phi') \frac{d\xi}{dx} \lambda' \nu', \end{aligned} \quad (14)$$

by (11). In these expressions we have to substitute the values above found for λ' and ν' , and perform the integrations according to θ , and to ϕ or ϕ' . It is convenient in evaluating the first term to use for $\lambda' \nu'$ the expression (13a) above, and in evaluating the second term to use the expression (13b).

To effect the integration according to ϕ or ϕ' , we reject from the product $\cos \phi$ and $\cos^3 \phi$, $\cos \phi'$ and $\cos^3 \phi'$, and for $\cos^2 \phi$ or $\cos^2 \phi'$ we

write $\frac{1}{2}$. We have then for the first term

$$\begin{aligned}
 & 2hcV^3 \int_0^{1^*} d\theta \int_0^{\pi} d\phi \sin \theta \cos \theta \lambda (-\nu \cos \theta + \sqrt{1-\nu^2} \sin \theta \cos \phi) \lambda' \nu' \frac{d\xi}{dz} \\
 = & 2hcV^3 \frac{d\xi}{dz} \int_0^{1^*} d\theta \int_0^{\pi} d\phi \sin \theta \cos \theta \lambda (-\nu \cos \theta + \sqrt{1-\nu^2} \sin \theta \cos \phi) \\
 & \times \left(-\nu \cos 2\theta + \sqrt{1-\nu^2} \sin 2\theta \cos \phi \right) \left(-\lambda \cos 2\theta - \frac{\lambda \nu}{\sqrt{1-\nu^2}} \sin 2\theta \cos \phi \right) \\
 = & -2hcV^3 \frac{d\xi}{dz} \lambda^3 \nu^2 \int_0^{1^*} d\theta \sin \theta \cos^2 \theta \cos^2 2\theta \\
 & + 2hcV^3 \frac{d\xi}{dz} \lambda^3 \nu^2 \frac{1}{2} \int_0^{1^*} d\theta \sin \theta \cos^3 \theta \sin^2 2\theta \\
 & - 2hcV^3 \frac{d\xi}{dz} \lambda^3 (1-\nu^2) \frac{1}{2} \int_0^{1^*} d\theta \sin^3 \theta \cos \theta \sin 2\theta \cos 2\theta \\
 & + 2hcV^3 \frac{d\xi}{dz} \lambda^3 \nu^2 \frac{1}{2} \int_0^{1^*} d\theta \sin^3 \theta \cos \theta \sin 2\theta \cos 2\theta \\
 = & 2hcV^3 \frac{d\xi}{dz} \frac{-11+12-4}{3.5.7} \lambda^3 \nu^3 \\
 & + 2hcV^3 \frac{d\xi}{dz} \frac{2}{3.5.7} \lambda^3.
 \end{aligned}$$

But $\bar{\lambda}^3 = \frac{1}{8}, \quad \bar{\lambda}^3 \nu^3 = \frac{1}{3.5};$

therefore

$$\bar{\lambda}^3 = 5\bar{\lambda}^3 \nu^3,$$

and our expression becomes

$$2hcV^3 \frac{d\xi}{dz} \frac{-11+12-4+10}{3.5.7} \bar{\lambda}^3 \nu^3,$$

or

$$\frac{1}{3.5} 2hcV^3 \frac{d\xi}{dz} \bar{\lambda}^3 \nu^3.$$

By symmetry, the second term gives

$$\frac{1}{3.5} 2hcV^3 \frac{d\zeta}{dx} \bar{\lambda}^3 \nu^3;$$

and so, given V ,

$$\begin{aligned}
 V^3 \bar{\lambda}' \nu' &= \bar{V}_x V'_x = \frac{1}{3.5} 2hcV^3 \bar{\lambda}^3 \nu^3 \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \\
 &= \frac{1}{3.5} 2hcV^3 \frac{1}{3.5} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right), \quad (15)
 \end{aligned}$$

since $\overline{\lambda^2 v^2} = \frac{1}{3.5};$

and
$$V^2 (\overline{\lambda' v'} - \overline{\lambda v}) = 2hcV^2 \frac{1}{3.5} \left(\frac{1}{3} + \frac{1}{3.5} \right) \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right). \quad (16)$$

21a. To find the rate of change with the time of $\overline{V_x V_x}$, given V , we multiply the last expression by the number of collisions which take place with given V per unit of volume and time, that is, by $2\pi c^3 \rho V$. The result is that, given V ,

$$\frac{d}{dt} \overline{V_x V_x} = 4\pi c^3 \rho V^4 \frac{1}{3.5} \left(\frac{1}{3} + \frac{1}{3.5} \right) \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right),$$

and, integrating for all values of V ,

$$\begin{aligned} \frac{d}{dt} \overline{V_x V_x} &= 4\pi c^3 \rho \int_0^\infty dV e^{-2hV^2} V^4 \frac{1}{3.5} \left(\frac{1}{3} + \frac{1}{3.5} \right) \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \\ &= \frac{1}{2h} \pi c^3 \rho \left(\frac{1}{3} + \frac{1}{3.5} \right) \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right). \end{aligned} \quad (17)$$

22. This being the value of $\frac{d}{dt} \overline{V_x V_x}$, what is the value of $\frac{d}{dt} \overline{uw}$?

Let u, v, w and u', v', w' be the component velocities of two colliding molecules, and, V being their half relative velocity, let U be the velocity of their common centre of gravity. Using V_x, V_y, V_z for the components of V , and U_x, U_y, U_z for the components of U , we have

$$u = V_x + U_x, \quad u' = -V_x + U_x,$$

$$v = V_y + U_y, \quad v' = -V_y + U_y,$$

$$w = V_z + U_z, \quad w' = -V_z + U_z;$$

therefore
$$uw + u'w' = 2(V_x V_x + U_x U_x).$$

And, as the change due to collision,

$$\partial(uw) + \partial(u'w') = 2\partial V_x V_x,$$

because U_x, U_y , and U_z are not altered by collision. It follows that on average of all molecules

$$\frac{d}{dt} \overline{V_x V_x} = \frac{d}{dt} \overline{uw},$$

and we may now write, as the result of collision,

$$\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right) \frac{d}{dt} \overline{uw} = \pi c^3 \rho \frac{1}{2h} \left(\frac{1}{3} + \frac{1}{3.5} \right) \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx} \right)^2. \quad (18)$$

23. We have next to consider the change in the term $uw \frac{d}{dt} \frac{d\xi}{dz}$ due to the variation of a by collisions. Consider two spheres in collision, the origin being the point of contact, and use the construction employed in Art. 15. The ordinates of their centres are z and $-z$, where

$$z = \frac{c}{2} (-v \cos \theta + \sqrt{1-v^2} \sin \theta \cos \phi).$$

For one a is increased, and for the other diminished, by $(\lambda' - \lambda) V$. Substituting for $\lambda' - \lambda$, introducing the factor $2\pi c^3 \rho V$, and integrating, we find that for each of the two molecules, as the result of collisions,

$$\begin{aligned} uw \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right) &= -\frac{16}{15} \pi c^3 \rho uw \lambda v V^2 \frac{1}{\Sigma f} \frac{1}{r} \frac{df}{dr} \\ &= -\frac{4}{15} \pi c^3 \rho 2u^2 w^2 \frac{1}{\Sigma f} \frac{1}{r} \frac{df}{dr} \\ &\quad \text{(because } \lambda v V^2 = \frac{1}{2} uw \text{ on average)} \\ &= \frac{4}{3 \cdot 5} \pi c^3 \rho \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right)^2, \text{ by Art. 15, (19)} \end{aligned}$$

and, adding 19 to 18, we find for the change in $\frac{dM}{dt}$ due to collision

$$\frac{\partial M}{\partial t} = \frac{2}{3} \pi c^3 \rho \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right)^2.$$

We interpret this as follows:—*As the result of collisions, molecules moving in a given direction, say x , are on average deflected towards that side where the average motion of the spheres, i.e., the stream, is for the time being in x . And so collisions tend to increase the stream.*

24. Now, referring to equation (I.), we see that $\frac{dM}{dt}$, which in the medium of material points was zero, has, when the spheres have finite diameter, become positive, namely,

$$\begin{aligned} \frac{dM}{dt} &= \Sigma A \iiint \epsilon^{-h(u^2+v^2+w^2)} du dv dw. uw \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right) - \Sigma \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right)^2 \\ &\quad + \Sigma \frac{2}{3} \pi c^3 \rho \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\xi}{dx} \right)^2, \quad \text{(II.)} \end{aligned}$$

of which the first two terms are together zero, as before. Therefore,

if in the system of finite spheres $\left(\frac{d\xi}{dz}\right)^2$, &c., have the same mean values as in the system of material points, $\frac{dM}{dt}$ is positive. But in stationary motion $\frac{dM}{dt}$ must be zero. How can we make it zero?

25. The solution is this. We must admit that the motion is not stationary if ξ, η, ζ , and therefore also $\frac{d\xi}{dz} + \frac{d\zeta}{dx}$, have the same average values which they have in the system of material points for which equation (I.) was proved. But in the system of finite molecules ξ has become $\xi + \xi'$, &c., and $\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2$ has become

$$\left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 + \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2.$$

That gives, by arranging the terms,

$$\begin{aligned} \frac{dM}{dt} = \Sigma A \iiint_{-\infty}^{+\infty} e^{-\lambda(u^2+v^2+w^2)} du dv dw \cdot uv \frac{d}{dt} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right) - \Sigma \frac{1}{2h} \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \\ + \Sigma \frac{1}{2} \pi c^2 \rho \frac{1}{2h} \left\{ \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 + \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2 \right\} - \Sigma \frac{1}{2h} \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2. \end{aligned} \quad (\text{III.})$$

The first two are together zero by (I.)

The remaining two terms can be made zero by suitably choosing the ratio

$$\left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2 : \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2.$$

We have, namely,

$$\kappa \left\{ \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2 + \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 \right\} = \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2,$$

or, if κ^2, κ^3 , &c., are neglected in comparison with κ ,

$$\left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)^2 : \left(\frac{d\xi}{dz} + \frac{d\zeta}{dx}\right)^2 :: \kappa : 1. \quad (20)$$

If we had introduced the factor $1 + \kappa$ into the first two terms of (III.), according to Art. 16, it would not affect the result, so long as κ^2 , &c., are neglected.

The term $uv \frac{d}{dt} \left(\frac{d\xi'}{dz} + \frac{d\zeta'}{dx}\right)$ is zero, because, as we shall see, Art.

32, ξ, η, ζ are independent of u, v, w .

26. It will be observed that the ratio so found is independent of the form of the functions ξ, η, ζ , that is, of the form of the function f of Art. 4. In order to confirm this result, let us consider the relation between ξ', η', ζ' , and the coefficients b of the products of velocities of different molecules in the index of e^{-hQ} .

27. By way of illustration let us suppose n molecules within a sphere of radius R , their velocities being distributed according to Maxwell's law e^{-hQ} , where Q is the sum of squares of the velocities, and let us impart to each molecule, in addition to the velocity which it has in that motion, the small velocity X' in x .

This being done, the chance that one of these molecules shall have velocity represented by lines drawn from the origin to some point or other within an element of volume $d\Omega$, whose centre is distant p from the origin in direction making the angle α with the axis of x , is

$$Ae^{-hQ^2}(1+2hpX'\cos\alpha)d\Omega.$$

The chance that another molecule shall have velocity represented by lines drawn from the origin to some point or other with an element of volume $d\Omega'$ distant q from the origin, in direction making the angle ϕ with p , is

$$Ae^{-hQ'^2}(1+2hqX'\cos\alpha\cos\phi+\sin\alpha\sin\phi\cos\epsilon),$$

where ϵ is the angle between the plane of p and q and the plane of p and x . The chance that both molecules shall have the velocities aforesaid is

$$A^2e^{-h(p^2+q^2)}d\Omega d\Omega'(1+2hpX'\cos\alpha)(1+2hqX'\cos\alpha\cos\phi+\sin\alpha\sin\phi\cos\epsilon).$$

Multiply this by $\sin\alpha d\alpha$, and integrate for all values of ϵ and α , and we find for the chance

$$A^2e^{-h(p^2+q^2)}d\Omega d\Omega'\left(1+\frac{4h^2}{3}X^2pq\cos\phi\right),$$

expressing now the chance that the velocities p and q , of two molecules, in whatever direction either is, shall make the angle ϕ with each other. Now let u, v, w be the components of p ; u', v', w' those of q . Then

$$p^2+q^2=u^2+v^2+w^2+u'^2+v'^2+w'^2,$$

$$d\Omega d\Omega' = du dv dw du' dv' dw',$$

$$pq\cos\phi = uu' + vv' + ww'.$$

Therefore, since, with these substitutions, the expression does not contain ϕ , it gives the chance that two molecules, both within the R sphere, shall respectively have velocities $u \dots u + du$, &c., in the form

$$A^3 e^{-h(u^2 + v^2 + w^2 + u'^2 + v'^2 + w'^2)} du \dots dw' \left\{ 1 + \frac{4h}{3} X^2 (uu' + vv' + ww') \right\},$$

that is, assuming X^2 , &c., to be small,

$$A^3 e^{-hQ'} du \dots dw',$$

in which $Q' = u^2 + v^2 + w^2 + u'^2 + v'^2 + w'^2 - \frac{4h}{3} X^2 (uu' + vv' + ww')$.

Evidently, if we take Y' and Z' into account, we shall have to substitute $X'^2 + Y'^2 + Z'^2$ for X'^2 in the last expression.

We see then that in the case now treated the coefficient of correlation has the form

$$b = -\frac{4h}{3} (X'^2 + Y'^2 + Z'^2), \quad (21)$$

or, since $\overline{X^2} + \overline{Y^2} + \overline{Z^2} = \frac{3}{2nh}$,

X, Y, Z denoting the velocities of the centre of inertia of the n molecules within the R sphere,

$$b = -\frac{2}{n} (X'^2 + Y'^2 + Z'^2) / (\overline{X^2} + \overline{Y^2} + \overline{Z^2}).$$

28. Let us now employ the converse method, namely, to find ξ'^2 , &c., in terms of the coefficients b , supposed given. We assumed, in Art. 4,

$$\xi = \frac{\sum a f}{\sum f},$$

whence $\frac{d\xi}{dz} = \sum a \frac{1}{\sum f} \frac{df}{dz}$.

Let us form the determinant

$$D = \begin{vmatrix} 2(\sum f)^2 & -2f_1 \sum f & -2f_2 \sum f & \dots \\ -2f_1 \sum f & (2+2f_1^2) & 2f_1 f_2 & \dots \\ -2f_2 \sum f & 2f_1 f_2 & (2+2f_2^2) & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

Then, as we found in Art. 7,

$$\bar{\xi} = \frac{D_{11}}{hD}.$$

29. In the system of finite spheres, if we assume b to have the same value for every pair of molecules considered (which we have to do if their relative positions are unknown), we find that every constituent of D_{11} is, owing to the introduction of b , multiplied by $\frac{2-b}{2}$. And therefore, b being very small, D_{11} becomes

$$D_{11} - \frac{n-1}{2} b D_{11}.$$

And so
$$\bar{\xi} + \bar{\xi}^2 = D_{11}/hD - \frac{n-1}{2} b D_{11}/hD$$

$$= \bar{\xi} - \frac{n-1}{2} b D_{11}/hD.$$

Therefore
$$\bar{\xi}^2 = -\frac{n-1}{2} b D_{11}/hD$$

$$= \frac{n-1}{4n} b,$$

whence
$$\bar{\xi}^2 + \bar{\eta}^2 + \bar{\xi}^2 = -\frac{3}{4h} b,$$

n being large, or
$$b = -\frac{4h}{3} (\bar{\xi}^2 + \bar{\eta}^2 + \bar{\xi}^2), \quad (22)$$

which agrees with Art. 27.

30. Next, let us assume b , the coefficient of correlation between the velocities of two molecules, to be a function of the distance r between the molecules to which it relates. And let it be required to find, on this hypothesis, the ratio

$$\bar{\xi}^2 : \bar{\xi}^2, \text{ or } \left(\frac{d\bar{\xi}}{dz} \right)^2 : \left(\frac{d\bar{\xi}}{dz} \right)^2.$$

For the system of finite spheres we shall have

$$Q = \Sigma a^2 + \Sigma \Sigma b_{pq} a_p a_q,$$

where b_{pq} is the value of b for the two molecules whose velocities are

$a_p, a_q, \&c.$, whence, substituting for a_n as in Art. 7,

$$Q = (1 + f_1^2 - b_{1n}f_1) a_1^2 + (1 + f_2^2 - b_{2n}f_2) a_2^2 + \&c. \\ + (2f_1f_2 + b_{12} - b_{1n}f_2 - b_{2n}f_1) a_1a_2 + \&c. \quad (23)$$

Then
$$\bar{\xi}^2 + \bar{\xi}^2 = \frac{D_{11} + \partial D_{11}}{hD} = \xi^2 + \Sigma b \frac{dD_{11}}{db} / hD,$$

or
$$\bar{\xi}^2 = \Sigma b \frac{dD_{11}}{db} / hD,$$

b being very small, so that its square and higher powers may be neglected, and, for the same reason, the variation of D may be neglected, as will be easily found.

Now, for the coefficient b_{pq} ,

$$\frac{dD_{11}}{db} = 2D_{11pq} = 2^{n-1}f_p f_q \text{ (by Art. 8),}$$

and so
$$\xi^2 = \frac{1}{hD} 2^{n-1} \Sigma \Sigma b_{pq} f_p f_q \\ = \frac{1}{hD} 2^{n-1} \Sigma f_p \Sigma b_{pq} f_q, \quad (24)$$

the summation being for every molecule of the system with every other.

31. Now let us assume

$$b_{pq} = -\frac{2}{3} \frac{c^5}{r^5}, \quad (25)$$

r being the distance between the two molecules p and q . Then $\Sigma f_p \Sigma b_{pq} f_q$ is represented by the integral

$$\frac{2}{3} \rho c^5 \iiint dx dy dz f_p \iiint \frac{f_q}{r^5} dx dy dz \\ = \frac{2}{3} \rho c^5 \iiint dx dy dz f_p \int_c^\infty 2\pi r^2 dr f / r^5,$$

2π being used for 4π because each pair is to be counted once.

It follows that, for all functions satisfying the conditions of Art. 4,

$$\Sigma \Sigma b_{\mu\nu} f_{\nu} f_{\mu} = 2^{n-1} \frac{2}{3} \pi c^3 \rho \Sigma f^2 = \kappa D_{11}, \quad (26)$$

$$\xi'^2 : \xi^2 :: \left(\frac{d\xi'}{dz} \right)^2 : \left(\frac{d\xi}{dz} \right)^2 :: \kappa : 1, \text{ as in (20), .}$$

which is independent of the form of the function f , provided that that function satisfies the conditions of Art. 4.

32. We may therefore now construct an auxiliary system containing the same number of molecules as the given system, each one of the former corresponding to one of the latter, and in which each molecule has at a given instant the same position which in the original system at that instant the corresponding molecule has. Attribute to the molecules in the auxiliary system so placed velocities at haphazard in such way that the mean square of the velocities in x , also in y and z respectively, shall be $\frac{1}{2h}$, where the ratio $\frac{h'}{h}$ has to be determined.

But the velocities attributed to any molecule in the auxiliary system shall be independent of the velocities which the corresponding molecule has at the given instant in the original system. Further, ξ' , η' , ζ' shall have for the auxiliary system the same meaning which ξ , η , ζ have for the original system, so that $\xi\xi' = 0$ on average, &c.

Then, since the form of ξ' , η' , ζ' is indifferent so long as they satisfy the conditions of Art. 4, we may take for ξ' , η' , ζ' the values of those functions derived from the auxiliary system. And, whatever be their forms, the ratios

$$\xi'^2/\xi^2 = h/h' = \left(\frac{d\xi'}{dz} \right)^2 / \left(\frac{d\xi}{dz} \right)^2,$$

and are the same for all functions ξ which satisfy the conditions.

Further, as a limiting case, we might take for ξ , η , ζ the component velocities of the common centre of inertia of any group of n molecules contained within a sphere of radius R : let them be X , Y , Z .

33. This, then, is the solution of the problem of stationary motion when the molecules are elastic spheres with finite diameter. Any group of contiguous spheres at any instant have greater energy of

motion of their common centre of inertia, and correspondingly less of relative motion, than they would have in the Maxwellian system as mere material particles, the entire kinetic energy being unchanged. The ratio $\xi^2 : \xi^2$ or $X^2 : X^2$ is, as we have seen, independent of n , the number of molecules in the group chosen.

34. Now, if Q be a sum of squares only, the energy of the motion of the common centre of inertia of the n spheres can on average have no other value than $\frac{1}{2} \frac{3}{2h}$, that is,

$$X^2 + Y^2 + Z^2 = \frac{1}{n} \frac{3}{2h}.$$

But we have seen that, in the system of finite spheres, $X^2 + Y^2 + Z^2$ has become $X^2 + X'^2 + Y^2 + Y'^2 + Z^2 + Z'^2$, and is therefore greater than $\frac{1}{n} \frac{3}{2h}$. Therefore, in the system of finite spheres, Q cannot be a sum of squares only—to prove which was my main object.

35. In the proof above given (Art. 31) I assumed $b = -\frac{2}{3} \frac{c^3}{r^3}$. For that purpose, however, $\frac{c^4}{r^4}$ would answer equally well. There is, however, another test to which we may subject the form of b chosen. It appears, namely, that, for a group of n molecules within a sphere of radius R , b , if it have the same value for every pair of molecules, varies as $\frac{1}{n}$, by Art. 29. Now the number of pairs that can be formed of n molecules is $\frac{n \cdot n - 1}{2}$. It follows that the sum of the coefficients b for every pair of molecules within the R sphere ought to vary as $n - 1$, that is, n being very great, as n , that is, to vary as R^3 , and therefore, if S be that sum, $\frac{dS}{dR} \propto R^2$. But now, if R becomes $R + dR$, S is altered only as follows, namely: for every molecule in the shell $4\pi R^2 dR$, we form a pair with every molecule within the sphere. The number of molecules within the shell varies as $4\pi R^2 dR$.

The sum of the number of pairs formed between any one of these and the molecules within the sphere is represented by the integral

$$2\pi \int_0^R r^2 \text{versin } PAC \, dr,$$

if $AP = r$, $AC = 2R$,

that is, $\int_0^{2R} dr r^3 \left(1 - \frac{r}{2R}\right)$.

Hence the sum of the coefficients b for all such pairs is, if $b = f(r)$,

$$\int_0^{2R} dr r^3 f(r) \left(1 - \frac{r}{2R}\right).$$

And therefore $\frac{dS}{dR} \propto 4\pi R^3 \int_0^{2R} dr r^3 f(r) \left(1 - \frac{r}{2R}\right)$,

but it ought to vary as $4\pi R^3$. Therefore b , or $f(r)$, must be so chosen that

$$\int_0^{2R} dr r^3 f(r) \left(1 - \frac{r}{2R}\right)$$

shall be independent of R . Now, if

$$f(r) = \frac{c^4}{r^4},$$

the integral contains $\log R$.

But, if $f(r) = -\frac{3}{2} \frac{c^3}{r^3}$,

the integral is proportional to

$$\frac{1}{2} c^3 \left(1 - \frac{c}{R}\right),$$

which for large values of R will answer the purpose.

36. As stated in the beginning of this paper, the law of distribution of velocities denoted by $e^{-\lambda Q}$ can hold good only so long as Q is necessarily positive, that is, incapable of being made negative, whatever values are attributed to the velocities u, v, w ; that is, so long as the determinant

$$D = \begin{vmatrix} 2 & b_{12} & b_{13} \\ b_{12} & 2 & b_{23} \\ \dots & \dots & \dots \end{vmatrix}$$

and each of its coaxial minors is positive. The limit is when $D = 0$. Now, in case of elastic spheres, b , and therefore D , appears as a function of the density only. That is because, in the case of elastic

spheres, the change of direction of the relative velocity due to collision, and therefore $\lambda'\nu' - \lambda\nu$ of Art. 20, depends only on θ and ϕ , and not on the magnitude of V .

In the case of the molecules being centres of repulsive force, let c be the distance at which when two molecules approach each other that force first becomes sensible, and call c the diameter of a molecule, and define θ, ϕ as in Art. 17. It is then easy to see that the change of direction of V between the beginning and end of an encounter depends on V as well as on θ and ϕ ; whence we may infer that, in this and in all cases where finite forces act between molecules, b and D are functions of h , *i.e.*, of the temperature, as well as of the density. It seems reasonable to expect that $D = 0$, the point at which the mathematical formula ceases to be applicable, would, if we could solve the problem, express that relation between density and temperature at which the gas changes its form and becomes liquid.

Concerning the Abstract Groups of Order $k!$ and $\frac{1}{2}k!$ Holohedrally Isomorphic with the Symmetric and the Alternating Substitution-Groups on k Letters. By ELIAKIM HASTINGS MOORE, of Chicago. Received November 24th, 1896. Read December 10th, 1896.

Introduction.

Every abstract group may be defined by a system of generators which are compounded in accordance with a table of generational relations. This fundamental theorem is due to Cayley.

So far as I know, no such abstract generational definitions of the groups abstractly equivalent respectively to the symmetric and the alternating substitution-groups on k letters have been given. Of course from any one such definition many other such definitions may easily be deduced.

In this paper I prove the following theorems:—

Theorem A.—The abstract group $G(k)$ ($k \geq 2$) defined by the $k-1$ generators

$$(1) \quad D_d \quad (d = 1, 2, \dots, k-1),$$