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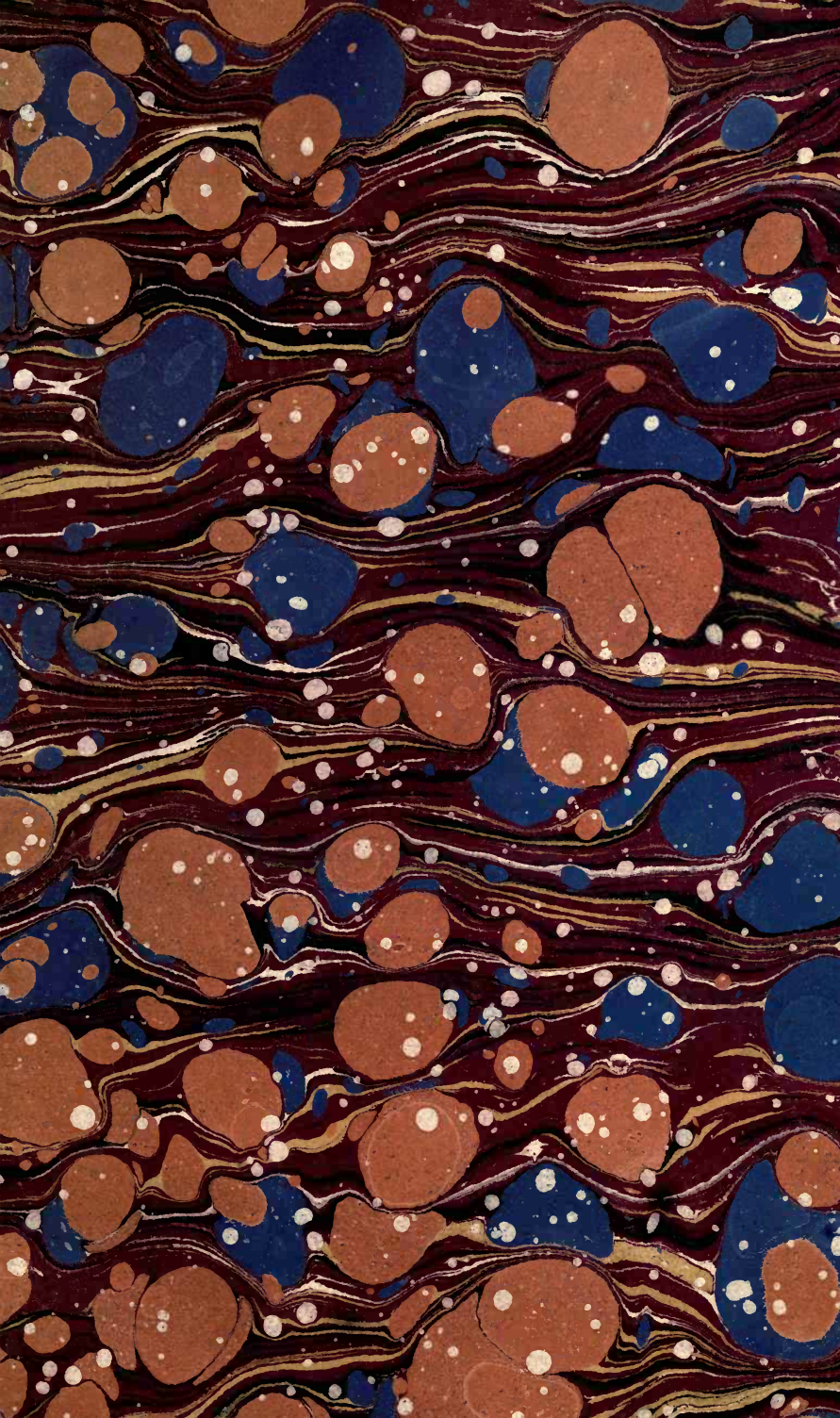

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# A TREATISE

ON THE

# KINETIC THEORY OF GASES

BY

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# PREFACE.

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

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

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

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

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

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

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

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

H. W. WATSON.

Berkswell Rectory,
Coventry, *Sept.* 17, 1876.

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

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# INTRODUCTION.

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

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

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

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

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

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

We thus meet with a new kind of regularity, the regularity of averages, a regularity which, when we are dealing with millions of millions of individuals, is so unvarying that we

are almost in danger of confounding it with absolute uniformity.

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

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

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

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

* MS. notes by Professor Clerk Maxwell.

point within the region at which the actual density of the matter had the value determined by our definition; for if the point were within a molecule the actual density would be much greater, and if it were not within a molecule the density would be zero.

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# KINETIC THEORY OF GASES.

## PROPOSITION I.

A VERY great number of smooth elastic spheres equal in every respect are in motion within a region of space of given volume, and therefore occasionally impinge upon each other with various degrees of relative velocity and in various directions. The space is so large in proportion to the sum of the volumes of the spheres that the average time during which any one sphere is moving free from contact with any other is infinitely greater than the average time during which it is in collision with some other sphere *. Required to find the law according to which the velocities must be distributed in order that such distribution may be permanent.

Let $N$ be the total number of spheres, and let

$$\chi(u, v, w)\, du\, dv\, dw$$

be the number of spheres whose component velocities parallel to the axes are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

respectively.

If we change the variables and make $c$ the resultant velocity, $\theta$ the inclination of $c$ to the axis of $z$, and $\phi$ that of the plane of $cz$ to the plane of $xz$, the expression given above will become

$$\chi(u, v, w)\, c^2 \sin\theta\, d\theta\, d\phi\, dc.$$

Let a spherical surface of radius unity be described round the origin as centre, and let us write $d\sigma$ for the element $\sin\theta\, d\theta\, d\phi$ on this spherical surface, then the last written expression becomes

$$\chi(u, v, w)\, c^2\, dc\, d\sigma.$$

* In the mathematical conception of a collision as an absolutely instantaneous phenomenon the proviso in the text is of course superfluous. An actual physical collision must take some time, however short, and the object of the proviso is to exclude the possibility, or rather to diminish indefinitely the probability, of the occurrence of cases in which the collision of one sphere with a second is not concluded before that with a third commences, and also to ensure that the number of colliding molecules at any instant is very much less than the number of molecules free from collision.

Since for the same magnitude of the resultant velocity all directions must be equally probable, it follows that the coefficient of $dc\,d\sigma$ in this expression must be a function of the resultant velocity $c$ only, and therefore the number of spheres having component velocities between $u$ and $u+du$, $v$ and $v+dv$, $w$ and $w+dw$ must be

$$\psi(c)\,du\,dv\,dw.$$

It is required, now, to find the form of $\psi$ in order that the value of this expression may be unaffected by collisions.

We assume that in the permanent state the distribution of the spheres throughout the space occupied by them is homogeneous in all respects; that is to say, on an average of any long time there are the same number of spheres in a given volume wherever that volume may be situated, and the law of distribution of velocities is the same throughout that volume as in the whole region under consideration.

Hence the number of pairs of spheres having component velocities between

$$u_1 \text{ and } u_1+du_1, \quad v_1 \text{ and } v_1+dv_1, \quad w_1 \text{ and } w_1+dw_1$$

for the one, and

$$u_2 \text{ and } u_2+du_2, \quad v_2 \text{ and } v_2+dv_2, \quad w_2 \text{ and } w_2+dw_2$$

for the other, and such that the lengths of the projections of their line of centres upon the axes are between

$$x \text{ and } x+dx, \quad y \text{ and } y+dy, \quad z \text{ and } z+dz,$$

must be proportional to

$$\psi(c_1)\,\psi(c_2)\,du_1\,dv_1\,dw_1\,du_2\,dv_2\,dw_2\,dx\,dy\,dz, \quad \ldots\ldots\ldots \quad \text{(A)}$$

where $c_1$ and $c_2$ are the resultant velocities.

Since the coefficient of $dx\,dy\,dz$ is independent of $x$, $y$, $z$, it follows that the number of pairs having their velocities between the above-mentioned limits and the projections of their line of centres between $x$ and $x+dx$, 0 and $dy$, 0 and $dz$ must be also represented by (A).

If $dy$ and $dz$ be infinitesimal in comparison with the diameter of any sphere, the lines of centres are parallel to the axis of $x$ and the velocity of approach of these centres is $u_1-u_2$.

If $d$ be the sum of the radii of any two of the spheres, or, what is the same thing in this case, the diameter of any one of them, then it follows that any pair of spheres having the $x$ component of their line of centres less than $d+(u_1-u_2)dt$ will encounter each other in the time $dt$; making therefore

$$x = d \quad \text{and} \quad dx = (u_1-u_2)\,dt,$$

it will follow that the number of collisions in time $dt$ of pairs of spheres with their lines of centres parallel to $x$ and velocities between the above limits is proportional to

$$\psi(c_1)\,\psi(c_2)\,du_1 \ldots dw_2\,dy\,dz\,(u_1-u_2)\,dt. \quad \ldots\ldots\ldots\ldots \quad (B)$$

After collision let the different quantities involved in (B) become $c_1'$, $c_2'$, $u_1'$, etc., while $x$, $y$, and $z$, $dy$ and $dz$ remain of course unchanged.

It follows therefore that if the values of these velocities and component velocities had originally been within the limits indicated by the accented letters with reversed signs, the spheres would, after collision, have passed into the original state as indicated by the unaccented letters. Call these states $E$ and $F$ respectively. For permanence of distribution therefore it is necessary that the number of collisions of pairs of spheres in state $E$ during the time $dt$ should be equal to the number of collisions of pairs in the state $F$ during the same time; and therefore that

$$\psi(c_1)\,\psi(c_2)\,du_1 \ldots dw_2\,dy\,dz\,(u_1-u_2) = \psi(c_1')\,\psi(c_2')\,du_1' \ldots dw_2'\,dy\,dz\,(u_2'-u_1').$$

Now

$$\begin{aligned} u_1' &= u_2, & \therefore\ du_1' &= du_2,\\ u_2' &= u_1, & du_2' &= du_1,\\ v_1 &= v_1', & dv_1 &= dv_1',\\ v_2 &= v_2', & dv_2 &= dv_2',\\ w &= w_1', & dw_1 &= dw_1',\\ w_2 &= w_2', & dw_2 &= dw_2'. \end{aligned}$$

Hence

$$du_1 \ldots dw_2\,dy\,dz\,(u_1-u_2) = du_1' \ldots dw_2'\,dy\,dz\,(u_2'-u_1');$$

$$\therefore\ \psi(c_1)\,\psi(c_2) = \psi(c_1')\,\psi(c_2'),$$

and

$$c_1^2+c_2^2 = c_1'^2+c_2'^2.$$

This functional equation may be integrated as follows. Let it be expressed in the form

$$\chi(c_1^2)\,\chi(c_2^2) = \chi(c_1'^2)\,\chi(c_2'^2),$$

and for $c_1^2$ and $c_2^2$ write $x$ and $x'$, and for $c_1'^2$ and $c_2'^2$ write $y$ and $y'$; then we have

$$\chi(x)\chi(x') = \chi(y)\chi(y'),$$

where $$x + x' = y + y';$$

$$\therefore \quad \chi(x)\chi(x') = \chi(y)\chi(x + x' - y);$$

therefore differentiating with respect to $x$ and $x'$,

$$\chi'(x)\chi(x') = \chi(y)\chi'(x + x' - y);$$

and $$\chi(x)\chi'(x') = \chi(y)\chi'(x + x' - y);$$

$$\therefore \quad \frac{\chi'(x)}{\chi(x)} = \frac{\chi'(x')}{\chi(x')};$$

that is, $$\frac{\chi'(x)}{\chi(x)} = \text{constant};$$

$$\therefore \quad \chi(x) = Ae^{-hx},$$

$$\therefore \quad \psi(c) = Ae^{-hc^2}.$$

Now the axis of $x$ may be taken in any direction. Whence it follows that this form of $\psi$ will ensure the permanence of distribution for all possible collisions.

Therefore the number of spheres with component velocities between $u$ and $u + du$, $v$ and $v + dv$, $w$ and $w + dw$

is $$Ae^{-hc^2}\,du\,dv\,dw,$$

or $$Ae^{-hc^2}c^2\,dc\,d\sigma.$$

employing the notation used above.

Integrating with respect to $d\sigma$ from 0 to $4\pi$ we find for the number of spheres with velocities between $c$ and $c + dc$ the expression

$$4\pi Ae^{-hc^2}c^2\,dc.$$

Again, since the number with component velocities between

$u$ and $u + du$, $v$ and $v + dv$, $w$ and $w + dw$

is $$Ae^{-h(u^2+v^2+w^2)}\,du\,dv\,dw,$$

or $$\sqrt[3]{A}e^{-hu^2}\,du\,\sqrt[3]{A}e^{-hv^2}\,dv\,\sqrt[3]{A}e^{-hw^2}\,dw,$$

it follows that the number of spheres having velocities intermediate between $u$ and $u + du$ parallel to any fixed line is

$$Ae^{-hu^2}\,du \int_{-\infty}^{\infty} e^{-hv^2}\,dv \int_{-\infty}^{\infty} e^{-hw^2}\,dw;$$

that is $$Ae^{-hu^2}\,du\,\frac{\pi}{h};$$

where $A$ may be determined by the equation

$$A\frac{\pi}{h}\int_{-\infty}^{\infty} e^{-hu^2}\,du = N;$$

or

$$A\frac{\pi^{\frac{3}{2}}}{h^{\frac{3}{2}}} = N;$$

and therefore

$$A = \frac{Nh^{\frac{3}{2}}}{\pi^{\frac{3}{2}}},$$

that is to say, the number of spheres having velocities between $c$ and $c+dc$ is

$$\frac{4Nh^{\frac{3}{2}}}{\sqrt{\pi}} \cdot e^{-hc^2}c^2\,dc.$$

If we multiply this expression by $c$, integrate the product with regard to $c$ from 0 to $\infty$ and divide by $N$, we find the mean velocity of all the spheres to be

$$\frac{2}{\sqrt{\pi h}}.$$

And, similarly, multiplying by $c^2$ instead of $c$, we find the mean square of the velocities to be

$$\frac{3}{2h},$$

and this is greater than the square of the mean velocity as it ought to be.

Before we proceed further it will be useful to make a formal statement of the method employed in the last proposition for denoting the velocities of molecules or material points.

Instead of drawing straight lines from each molecule indicating the magnitude and direction of the velocity of that molecule, we draw all such straight lines for all molecules from any assumed point taken as the origin.

This method is very useful when, as in investigations like the present, we wish to compare the simultaneous velocities of different molecules as well as the successive velocities of each molecule separately.

We thus obtain a figure every point of which corresponds to one of our molecules, the velocity of that molecule is represented in magnitude and direction by a line drawn from the origin to the corresponding point, and the relative velocity of any two

molecules is also represented by the line joining the points corresponding to these two molecules. If the system have a common velocity, then we must suppose the position of the new origin of the diagram of velocities with respect to the old origin to be so chosen as to represent this velocity.

In studying the motion of the system it is found convenient to divide the molecules into groups according to their velocities, those molecules whose velocities lie within certain limits with respect to magnitude and direction being placed in the same group.

In the velocity diagram these molecules are indicated at once by the points which correspond to them being included within a certain small region or elementary volume of the diagram, the boundary of this region corresponding to the given limits of velocity.

Thus, in the proposition just now considered, the state $E$ might be described as that in which the velocity points are situated within the elementary volume

$$du\,dv\,dw \quad \text{or} \quad c^2 \sin\theta\, d\theta\, d\phi\, dc$$

of the diagram of velocities.

We may also conveniently make use of the term velocity-density to indicate the result of dividing the number of molecules whose velocities lie within the given limits by the volume of the corresponding region in the diagram of velocities.

## PROPOSITION II.

Let the $N$ elastic spheres of the last proposition be replaced by two sets, one of $N$ spheres each having mass $m$, and the other of $N'$ spheres each having mass $m'$, and let us find the law of distribution of the velocities of the $N$ and $N'$ spheres respectively.

Exactly as in the last proposition, it may be proved that the number of $N$ spheres whose component velocities parallel to the axes are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

respectively must be

$$\psi(c)\, du\, dv\, dw,$$

where $$c^2 = u^2 + v^2 + w^2;$$

and that the number of the $N'$ spheres whose component velocities are intermediate between

$$u' \text{ and } u'+du', \quad v' \text{ and } v'+dv', \quad w' \text{ and } w'+dw'$$

must be $$\psi_1(c')\,du'\,dv'\,dw';$$

and that the number of collisions in time $dt$ between pairs of spheres, one from each set, with lines of centres parallel to the axis of $x$ and component velocities between the above limits respectively, must be proportional to

$$\psi(c)\,\psi_1(c')\,du\,dv\,dw\,du'\,dv'\,dw'\,(u-u')\,dt \quad \ldots\ldots\ldots\ldots\ldots\ldots (A)$$

If the component velocities of these spheres after collision be between

$$U \text{ and } U+dU, \quad V \text{ and } V+dV, \quad W \text{ and } W+dW,$$
$$U' \text{ and } U'+dU', \quad V' \text{ and } V'+dV', \quad W' \text{ and } W'+dW'$$

respectively, then, by the reasoning employed in the last case, we must have

$$\psi(c)\,\psi_1(c')\,du \ldots dw'\,(u-u') = \psi(C)\,\psi_1(C')\,dU \ldots dW'\,(U'-U), \ldots (B)$$

where $$V=v, \quad W=w, \quad V'=v', \quad W'=w',$$

$$U = u - \frac{2m'}{m+m'}(u-u'),$$

$$U' = u' + \frac{2m}{m+m'}(u-u');$$

whence we get $$mC^2+m'C'^2 = mc^2+m'c'^2,$$

$$\frac{dU}{du}\frac{dU'}{du} - \frac{dU}{du}\cdot\frac{dU'}{du'} = \frac{(m-m')^2}{(m+m')^2} + \frac{4mm'}{(m+m')^2} = 1;$$

and also

$$dV = dv, \quad dW = dw, \quad dV' = dv', \quad dW' = dw',$$
$$U'-U = u-u',$$

and $$dU\,dU' = du\,du'\left(\frac{dU}{du'}\frac{dU'}{du} - \frac{dU}{du}\frac{dU'}{du'}\right) = du\,du'.$$

So that equation (B) reduces to

$$\psi(c)\,\psi_1(c') = \psi(C)\,\psi_1(C'),$$

where $$mc^2+m'c'^2 = mC^2+m'C'^2.$$

A functional equation of which, as before, the solution may be shewn to be

$$\psi(c) = Ae^{-h\frac{mc^2}{2}} \quad \text{and} \quad \psi_1(c') = Be^{-h\frac{m'c'^2}{2}}.$$

It must be remembered that $h$ is here a constant of different dimensions from the $h$ of the last proposition.

Since the axis of $x$ may be taken in any direction, it follows that these forms of $\psi$ and $\psi_1$ will ensure the permanence of distribution as far as collisions between spheres of two different sets are concerned, and we have already proved that they will ensure that permanence so far as collisions between spheres of the same set are concerned; therefore it follows that the number of the $N$ spheres whose component velocities are intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

must be $$A e^{-h\frac{mc^2}{2}}\, du\, dv\, dw,$$

where $$c^2 = u^2+v^2+w^2;$$

and the number of the $N'$ spheres whose component velocities are intermediate between

$$u' \text{ and } u'+du', \quad v' \text{ and } v'+dv', \quad w' \text{ and } w'+dw'$$

must be $$B e^{-h\frac{m'c'^2}{2}}\, du'\, dv'\, dw',$$

where $$c'^2 = u'^2+v'^2+w'^2;$$

and it is clear that the same reasoning would hold whatever number of sets of such spheres the space might contain.

Applying the results of the last proposition, and writing

$$\frac{mh}{2}, \quad \frac{m'h}{2}$$

instead of $h$ we get

$$A = \frac{N}{\pi^{\frac{3}{2}}}\cdot\left(\frac{mh}{2}\right)^{\frac{3}{2}}, \quad B = \frac{N'}{\pi^{\frac{3}{2}}}\cdot\left(\frac{m'h}{2}\right)^{\frac{3}{2}};$$

and so on for any other sets which the region may contain.

We also find that the mean velocity of each of the $N$ spheres is

$$\frac{2}{\sqrt{\pi}}\cdot\sqrt{\frac{2}{mh}},$$

and similarly for the remaining sets of spheres.

Also the mean square of the velocity of each of the $N$ spheres is

$$\frac{3}{2}\cdot\frac{2}{mh},$$

and the mean vis viva

$$\frac{3}{2h},$$

the last result being the same for each set of spheres.

## PROPOSITION III.

On the hypothesis of the last proposition to find the number of pairs of spheres, one being taken from the $N$ set and the other from the $N'$ set, whose relative velocities lie between given limits, and the number of collisions in unit of time and unit of volume between these sets of spheres.

Using the results of the last proposition, writing $\frac{1}{a^2}$ for $\frac{hm}{2}$ and $\frac{1}{\beta^2}$ for $\frac{hm'}{2}$, and supposing the volume of the region considered to be the unit of volume, we find that the number of spheres of the $N$ set which have their component velocities parallel to $x$ between the limits $u$ and $u+du$ is

$$\frac{N}{a\sqrt{\pi}} \cdot e^{-\frac{u^2}{a^2}} du; \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (A)$$

and that the number of spheres of the $N'$ set which have their component velocities parallel to $x$ between the limits $u+U$ and $u+U+dU$ is

$$\frac{N'}{\beta\sqrt{\pi}} \cdot e^{-\frac{(u+U)^2}{\beta^2}} dU; \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (B)$$

and therefore the number of pairs of spheres fulfilling the above-mentioned conditions is

$$\frac{NN'}{a\beta\pi} \cdot e^{-\left\{\frac{u^2}{a^2} + \frac{(u+U)^2}{\beta^2}\right\}} du\, dU.$$

Integrating with respect to $u$ from $-\infty$ to $+\infty$, we find for the total number of pairs of spheres whose relative velocity parallel to $x$ lies between $U$ and $U+dU$ the expression

$$\frac{NN'}{\sqrt{a^2+\beta^2}} \cdot \frac{1}{\sqrt{\pi}} e^{-\frac{U^2}{a^2+\beta^2}} dU. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (C)$$

Comparing (C) with (A) we see that the distribution of relative velocities follows a law of the same form as that of absolute velocities, and therefore that the mean relative velocity is the square root of the sum of the squares of the mean absolute velocities in the two systems, and the mean square of the relative velocity is the sum of the mean squares of the absolute velocities.

It follows also of course that the number of pairs of spheres, one from each set, whose relative velocities lie between $r$ and $r+dr$ is

$$NN' \frac{4}{\sqrt{\pi}(\alpha^2+\beta^2)^{\frac{3}{2}}} \cdot e^{-\frac{r^2}{\alpha^2+\beta^2}} r^2 dr;$$

or, restoring to $\alpha$ and $\beta$ their values,

$$NN' \frac{\sqrt{2}}{\sqrt{\pi}} \cdot \frac{(mm'h)^{\frac{3}{2}}}{(m+m')^{\frac{3}{2}}} \cdot e^{-\frac{r^2 mm' h}{2(m+m')}} r^2 dr.$$

We proceed now to find the number of collisions in unit of time and volume between the spheres of the $N$ set and those of the $N'$ set.

Suppose a number $N$ of equal spheres at rest to be distributed in any manner throughout a unit of volume, and suppose that another sphere moves among them with the velocity $r$. If a tubular surface be described having for axis the path of the centre of this moving sphere, and for its radius $s$, or the sum of the radii of the moving sphere and one of the stationary spheres, the volume of the surface thus generated in a unit of time by the moving sphere will be $\pi r s^2$. Hence the chance of the moving sphere colliding with any one of the fixed spheres in a unit of time must be $\pi r s^2$, and the number of collisions in unit of time between the moving sphere and stationary spheres must be $N\pi r s^2$.

The same results would hold good if we replaced the stationary spheres by spheres moving with a common velocity and the moving sphere had a velocity $r$ relative to each of them, that is to say, the chance of collision in unit of time between the last-mentioned sphere and any one of the former-mentioned spheres would be $\pi r s^2$.

Suppose now that there are two sets of $N$ and $N'$ spheres in the unit of volume, and that the number of pairs of spheres (one being taken from each set) whose relative velocities are between $r$ and $r+dr$ is $nn'$, then, if $s$ be the sum of the radii of each pair, it will follow that the chance of a collision between any pair in unit of time is $\pi r s^2$, and therefore that the total number of collisions in unit of volume and unit of time is $nn'\pi r s^2$.

But we have already seen that $nn'$ is equal to

$$NN' \frac{4}{\sqrt{\pi}(a^2+\beta^2)^{\frac{3}{2}}} e^{-\frac{r^2}{a^2+\beta^2}} r^2 dr,$$

$N$ and $N'$ being the total number of spheres of each set in unit-volume, and $a^2$ and $\beta^2$ being written for $\frac{2}{mh}$ and $\frac{2}{m'h}$, as before.

Hence the number of collisions in unit-time between pairs of spheres whose relative velocity lies between $r$ and $r+dr$ is

$$NN' \frac{4\sqrt{\pi}}{(a^2+\beta^2)^{\frac{3}{2}}} \cdot s^2 r^3 e^{-\frac{r^2}{a^2+\beta^2}} dr;$$

or

$$NN' \frac{\sqrt{2}}{\sqrt{\pi}} \cdot \frac{(mm'h)^{\frac{3}{2}}}{(m+m')^{\frac{3}{2}}} \cdot s^2 r^3 e^{-\frac{r^2 mm' h}{2(m+m')}} dr.$$

Integrating from $r = 0$ to $r = \infty$, we get

$$2NN' \sqrt{\pi} \cdot \sqrt{a^2+\beta^2}\, s^2$$

or

$$2NN\sqrt{\pi} \sqrt{\frac{2(m+m')}{mm'h}} \cdot s^2$$

for the number of collisions in unit of time which take place in unit of volume between spheres of the $N$ and $N'$ sets.

The number of collisions in the same time and volume between spheres of the $N$ set is therefore

$$2N^2 \sqrt{\pi} \sqrt{2a^2} \cdot s_1^2,$$

or

$$\frac{4N^2\sqrt{\pi}}{\sqrt{mh}} \cdot s_1^2;$$

and between spheres of the $N'$ set the number is

$$2N'^2 \sqrt{\pi} \sqrt{2\beta^2}\, s_2^2,$$

or

$$\frac{4N'^2\sqrt{\pi}}{\sqrt{m'h}} \cdot s_2^2.$$

Also, since the mean velocities in the two systems are

$$\frac{2a}{\sqrt{\pi}} \text{ and } \frac{2\beta}{\sqrt{\pi}},$$

it follows that if $l_1$ be the mean distance travelled by a sphere of the $N_1$ set between each collision with a sphere of its own set and $l_2$ the corresponding mean distance for the second set, then

$$\frac{1}{l_1} = \pi N_1 \sqrt{2}\, s_1^2 \quad \text{and} \quad \frac{1}{l_2} = \pi N_2 \sqrt{2}\, s_2^2,$$

$s_1$ and $s_2$ being diameters of spheres of the two sets.

Also, if $\lambda_1$ be the mean distance travelled by a sphere of the $N_1$ set without any collision whatever,

$$\frac{1}{\lambda_1} = \pi N_1 \sqrt{2}\, s_1^2 + \pi N_2 \frac{\sqrt{\alpha^2+\beta^2}}{\alpha} {}_1s_2^2 + \pi N_3 \frac{\sqrt{\alpha^2+\gamma^2}}{\alpha} {}_1s^2{}_3 + \&c.;$$

where ${}_1s_r$ is sum of radii of spheres of the $N_1$ and $N_r$ sets, with a similar expression for the mean distance travelled by a sphere of any other set.

The next case to be considered will be that in which there are any number of sets of spheres as in the last proposition, but acted on by any given impressed forces tending to fixed centres, and therefore capable of being expressed as the space variations of a potential function. Before treating of this case it will be necessary to prove the following general proposition, due originally to Dr. Ludwig Boltzmann and subsequently modified by Professor Maxwell.

Let $p_1 \dots p_n$ be the generalized coordinates, and $q_1 \dots q_n$ the corresponding momenta of any conservative system at any given time, and let $P_1 \dots P_n$, $Q_1 \dots Q_n$ be the corresponding quantities after any interval.

Let the action from the initial to the final state expressed in terms of the initial and final coordinates ($p$ and $P$) and the energy $E$ be $A$.

Then, by Thompson and Tait, vol. i, p. 236,

$$q_r = -\frac{dA}{dp_r} \text{ for initial state,} \quad Q_r = \frac{dA}{dP_r} \text{ for final state.}$$

Let $f(p, q)$ be any given function of the $p$'s and $q$'s, and let us change the variables in the multiple differential

$$f(p, q)\, dp_1 \dots dp_n\, dq_1 \dots dq_n,$$

from the $p$'s and $q$'s to the $p$'s and $P$'s, i.e. from the $2n$ initial coordinates and momenta to the $2n$ initial and final coordinates.

The expression then becomes

$$f_1(p, P)\, dp_1 \dots dp_n\, dP_1 \dots dP_n \Delta;$$

where $\Delta$ is the functional determinant

$$\Sigma \pm \left(\frac{dq_1}{dP_1} \cdots \frac{dq_n}{dP_n}\right),$$

or

$$\begin{vmatrix} \frac{dq_1}{dP_1} & \cdots & \frac{dq_1}{dP_n} \\ \frac{dq_2}{dP_1} & \cdots & \frac{dq_2}{dP_n} \\ \vdots & & \vdots \\ \frac{dq_n}{dP_1} & \cdots & \frac{dq_n}{dP_n} \end{vmatrix}.$$

Now $$\frac{dq_r}{dP_s} = -\frac{d^2A}{dp_r\,dP_s} = -\frac{dQ_s}{dp_r};$$

$$\therefore \quad \Sigma \pm \left(\frac{dq_1}{dP_1} \cdots \frac{dq_n}{dP_n}\right) = -\Sigma \pm \left(\frac{dQ_1}{dp_1} \cdots \frac{dQ_n}{dp_n}\right);$$

$$\therefore\ f(p,q)\,dp_1 \ldots dp_n dq_1 \ldots dq_n = f_1(p,P)\,dp_1 \ldots dp_n dP_1 \ldots dP_n \Sigma\left(\pm \frac{dq}{dP}\right),$$

$$= f_1(p,P)\,dp_1 \ldots dp_n dP_1 \ldots dP_n \Sigma\left(\pm \frac{dQ}{dp}\right),$$

$$= F(P,Q)\,dP_1 \ldots dP_n\,dQ_1 \ldots dQ_n;$$

where $F(P,Q)$ and $f(p,q)$ are equal to each other;

$$\therefore \quad dp_1 \ldots dp_n\,dq_1 \ldots dq_n = dP_1 \ldots dP_n\,dQ_1 \ldots dQ_n;$$

or the product of the differentials remains the same in value after the change of variables.

## PROPOSITION IV.

Let there be any number of sets of spheres as in the last proposition, and let them be acted on by any forces passing through the centres of the spheres tending to fixed centres and functions of the distances of the centres of the spheres from the centres of force.

We can no longer assume that the chance of velocities in all directions is the same, as we did in the first two propositions; in other words, we cannot prove, as we did in Proposition I, that the number of spheres of any set having component velocities intermediate between

$$u \text{ and } u+du, \quad v \text{ and } v+dv, \quad w \text{ and } w+dw$$

is $$\psi(c)\,du\,dv\,dw,$$

Let us assume then that the number of spheres of any one set, as the first set, at any time $t$, having component velocities

between the above-mentioned limits and having the coordinates of their centres intermediate between

$$x \text{ and } x+dx, \quad y \text{ and } y+dy, \quad z \text{ and } z+dz,$$

is $$\psi(x, y, z, u, v, w)\, dx\, dy\, dz\, du\, dv\, dw.$$

We must in the first place determine the form of

$$\psi(x, y, z, u, v, w),$$

so that it may be independent of $t$, i.e. so that apart from collisions, the number of spheres of the first set, having their positions and velocities between the limits stated above, may always be the same function of the variables $x$, $y$, $z$, $u$, $v$, and $w$.

Let any sphere whose position and velocity are within the limits defined above be said to be in the state A, and after an interval of time $\tau$ let it pass into the state B, such that the coordinates and component velocities are intermediate between

$$X \text{ and } X+dX, \text{ \&c., \&c. ..... } W \text{ and } W+dW.$$

For facility of reference it will be better to denote the states A and B by the subjoined schemes:—

*Coordinates of centre between limits.*

STATE A. $x$ and $x+dx$, $y$ and $y+dy$, $z$ and $z+dz$;

STATE B. $X$ and $X+dX$, $Y$ and $Y+dY$, $Z$ and $Z+dZ$;

*Component velocities between limits.*

STATE A. $u$ and $u+du$, $v$ and $v+dv$, $w$ and $w+dw$;

STATE B. $U$ and $U+dU$, $V$ and $V+dV$, $W$ and $W+dW$;

with corresponding changes for the accented variables.

It follows that the number of spheres in the state A at time $t$ must be equal to the number in the state B at time $t+\tau$; and therefore, if the form of $\psi$ be independent of the time,

$$\psi(x, y, z, u, v, w)\, dx \ldots dw = \psi(X, Y, Z, U, V, W)\, dX \ldots dW.$$

But by the last proposition

$$dx \ldots dw = dX \ldots dW,$$

and therefore $$\psi(x \ldots w) = \psi(X \ldots W).$$

Now let $$\phi_1 = a_1, \quad \phi_2 = a_2, \text{ \&c.}$$

be any equations between the variables $x \ldots w$, obtained by the

elimination of $t$ from the integrals of the equations of motion of any one sphere. Then we know that

$$f(\phi_1, \phi_2, \&c.)$$

remains constant throughout the motion.

If therefore $\psi(x \dots w)$ be of the form

$$\psi(\phi_1, \phi_2, \&c.),$$

in other words, if $x, \dots w$ enter into $\psi$ only by entering into $\phi_1$, $\phi_2$, &c., we shall have

$$\psi(x \dots w) = \psi(X \dots W).$$

Hence it follows that, for permanence of distribution independently of collisions, the number of spheres of the $N$ set having the coordinates of their centres and their component velocities intermediate between

$$x \text{ and } x+dx \dots w \text{ and } w+dw$$

must be $$\psi(\phi_1, \phi_2, \&c.)\, dx \dots dw.$$

And similarly, the number of spheres of the $N'$ set having the coordinates of their centres and their component velocities intermediate between

$$x' \text{ and } x'+dx' \dots w' \text{ and } w'+dw'$$

must be $$\psi_1(\phi_1', \phi_2', \&c.)\, dx' \dots dw'.$$

We must now determine the forms of $\psi$ and $\psi_1$ in order that this law of distribution may be unaffected by collisions.

By reasoning in all respects the same as in Proposition II we are led to the equation

$$\psi(\phi_1, \phi_2, \&c.)\, \psi_1(\phi_1', \phi_2', \&c.) = \psi(\Phi_1, \Phi_2, \&c.)\, \psi_1(\Phi_1', \Phi_2', \&c.),$$

with the equation

$$\frac{mc^2}{2} + \frac{m'c_1'^2}{2} = \frac{mC^2}{2} + \frac{m'C_1'^2}{2}.$$

Also, since the coordinates of the centres are unaffected by collision, it follows that, if $\chi$ and $\chi_1$ be the potentials of the impressed forces on the two spheres before collision, and $\mathrm{X}$ and $\mathrm{X}_1$ after collision,

$$\chi = \mathrm{X} \text{ and } \chi_1 = \mathrm{X}_1,$$

or $$\chi + \frac{mc^2}{2} + \chi_1 + \frac{m'c_1'^2}{2} = \mathrm{X} + \frac{mC^2}{2} + \mathrm{X}_1 + \frac{m'C_1'^2}{2}.$$

Now the only condition limiting $\phi_1$, $\phi_2$, &c. is that they be equations obtained by eliminating $t$ from any of the integrals

of the equations of motion of the sphere, and the equation of conservation of energy, or

$$\chi + \frac{mc^2}{2} = a,$$

is such an equation, hence $\psi$ may be of the form

$$\psi\left(\chi + \frac{mc^2}{2}\right).$$

Assuming this form for $\psi$, we get for our condition of permanence

$$\psi\left(\chi + \frac{mc^2}{2}\right)\psi_1\left(\chi' + \frac{m'c'^2_1}{2}\right) = \psi\left(\mathrm{X} + \frac{mC^2}{2}\right)\psi_1\left(\mathrm{X}' + \frac{m'C'^2}{2}\right),$$

where $$\chi + \frac{mc^2}{2} + \chi' + \frac{m'c'^2_1}{2} = \mathrm{X} + \frac{mC^2}{2} + \mathrm{X}' + \frac{m'C'^2}{2}.$$

A functional equation of which the solution has been proved to be

$$\psi = Ae^{-h\left(\chi + \frac{mc^2}{2}\right)},$$

$$\psi_1 = Be^{-h\left(\chi_1 + \frac{m'c'^2_1}{2}\right)};$$

whence we conclude that the number of spheres of the set $N$ having the coordinates of their centres and their component velocities intermediate between

$$x \text{ and } x+dx \ldots w \text{ and } w+dw$$

must be $$Ae^{-h\left(\chi + \frac{mc^2}{2}\right)}dx\,dy\,dz\,du\,dv\,dw,$$

and the number of the set $N'$ similarly circumstanced must be

$$Be^{-h\left(\chi + \frac{m'c^2}{2}\right)}dx\,dy\,dz\,du\,dv\,dw;$$

and so on for all the remaining sets of spheres.

Since the number of spheres of the $N$ set whose centres and velocity points lie within the elementary volumes $dx\ dy\ dz$ and $du\ dv\ dw$ in the neighbourhood of the points $x, y, z$, and $u, v, w$, respectively is

$$Ae^{-h\left(\chi + \frac{mc^2}{2}\right)}du\,dv\,dw\,dx\,dy\,dz; \quad \ldots\ldots\ldots\ldots\ldots \quad (a)$$

where $c$ is the distance of the point $u, v, w$, from the origin in the velocity diagram, with similar expressions for each of the other sets, it follows that the law of distribution of the velocities and positions of each set of spheres is independent of the co-existence of the other sets in the region under consideration.

If we write, as before, $c^2\,dc\,d\sigma$ for the elementary volume $du\,dv\,dw$, the expression $(\alpha)$ becomes

$$Ae^{-h\chi}\,dx\,dy\,dz\,.\,e^{-\frac{hmc^2}{2}}c^2\,dc\,d\sigma.$$

Integrating with regard to $\sigma$ from 0 to $4\pi$ and with regard to $c$ from 0 to $\infty$, we find that the total number of spheres of any one set whose centres are situated within the elementary volume $dx\,dy\,dz$ is given by an expression of the form

$$Be^{-h\chi}dx\,dy\,dz. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\beta)$$

That is to say, $\rho$, or the density of the $N$ set matter in the neighbourhood of the point $x$, $y$, $z$, is

$$mBe^{-h\chi}.$$

Again, if we integrate the same expression $(\alpha)$ with regard to $x$, $y$, and $z$ for all values corresponding to the region under consideration, we find that the total number of spheres of the $N$ set whose velocity points are situated within the element $dc\,d\sigma$ is, as in the last case, given by an expression of the form

$$Ce^{-\frac{hmc^2}{2}}c^2\,dc\,d\sigma; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\gamma)$$

whence it follows that so long as the radius vector in the velocity diagram is constant, all directions of that radius vector are equally probable, or that the distribution of velocities is the same in all directions; and this being true of each set of spheres, taken separately, is of course true of the sum total of the spheres in the region under consideration.

Again, integrating $(\gamma)$ with regard to $\sigma$ from 0 to $4\pi$, we see that the number of spheres of the $N$ set having velocities between $c$ and $c+dc$ is

$$4\pi\,Ce^{-\frac{hmc^2}{2}}c^2dc;$$

whence, as in the last case, we obtain the following results, viz.

The mean velocity of these spheres is $\dfrac{2\sqrt{2\pi}}{\sqrt{mh}}$;

The mean square of the velocities is $\dfrac{3}{mh}$;

The mean vis viva is $\ldots\ldots\ldots\ldots\ldots\ldots \dfrac{3}{2h}$.

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And since the last expression involves only the constant $h$ which is common to all the sets of spheres, it follows that the mean vis viva of the spheres in every set is the same, and therefore equal to the mean vis viva of all the spheres in the region under consideration.

## PROPOSITION VI.

A number of sets of elastic spheres are moving about in a given region, as in the last proposition, required to find the action exerted by one portion of the medium on another, or the *pressure*, in the neighbourhood of any point.

Let us assume that the surface of separation of the two portions of the medium is a plane perpendicular to the axis of $x$, and since the distribution and motion of the spheres of any one set have been proved to be completely independent of the coexistence of the spheres of the remaining sets, let us confine our attention, for the present, to what we have called the $N$ set of spheres.*

Suppose that there are $dN$ such spheres, per unit volume, in the neighbourhood of the point $x$, $y$, $z$, whose component velocities parallel to the axis of $x$ are between $u$ and $u+du$.

The number of these spheres which cross the elementary area $dy\,dz$ in time $dt$ will be the same as the number of the $dN$ spheres whose centres are situated within the elementary parallelopiped $dx\,dy\,dz$ in which $dx$ is equal to $udt$, and this number is

$$dN\,.\,u\,.\,dy\,dz\,dt.$$

Each of these spheres carries across with it a momentum parallel to the axis of $x$ equal to $mu$; the total momentum parallel to the axis of $x$ transferred across $dy\,dz$ in the time $dt$ is therefore

$$m\,dN\,u^2\,dy\,dz\,dt.$$

If $u$ be positive this is positive momentum transferred from the negative to the positive side of the plane $yz$, and if $u$ be negative this is negative momentum similarly transferred from the positive to the negative side of the same plane.

* That is to say, the set whereof the number contained in the given region is $N$.

In either case the result is that by the mere motion of these spheres across the area $dy\,dz$ the positive momentum parallel to the axis of $x$ is diminished by the quantity $m\,dN\,u^2\,dy\,dz\,dt$ on the negative side of the plane $yz$ and increased by the same quantity on the positive side of that plane in the time $dt$.

Hence the result is the same as a transference of positive momentum parallel to the axis of $x$ in time $dt$ across the area $dy\,dz$ equal to $m\,dy\,dz\,dt\,\Sigma_{-\infty}^{\infty} u^2\,dN$, that is equal to

$$dy\,dz\,dt\,\rho\overline{u^2}; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (a)$$

where $\rho$ is the density of the $N$ set matter at the point $x, y, z$, and $\overline{u^2}$ is the mean square of the velocities parallel to the axis of $x$.

But either by integration or general reasoning it is easily seen that $\overline{u^2}$ is equal to $\frac{v^2}{3}$, where $v^2$ is the mean square of the velocities of the $N$ set of spheres, and is equal, as we have seen, to $\frac{3}{mh}$.

Hence there is a transference of positive momentum from the negative to the positive side of the plane $yz$ across the area $dy\,dz$ in the time $dt$ equal to

$$\rho\,dy\,dz\,dt\,\frac{v^2}{3}, \text{ or to } \frac{\rho\,dy\,dz\,dt}{mh}.$$

Each separate sphere (whose component velocities are $u$, $v$, and $w$) carries across the same plane momenta parallel to the axes of $y$ and $z$ equal to $mv$ and $mw$ respectively, so that in the time $dt$ there are carried across the elementary area $dy\,dz$ momenta parallel to the axes of $y$ and $z$ equal to $\Sigma\,muv\,dy\,dz\,dt$ and $\Sigma\,muw\,dy\,dz\,dt$ respectively.

It is clear from the symmetrical distribution of the velocities that $\Sigma\,muv$ and $\Sigma\,muw$ are each equal to zero.

Therefore the resultant mutual action of the two portions of the medium across the elementary area $dy\,dz$ in the time $dt$ is the transference of the momentum $\rho\,dy\,dz\,dt\,\frac{v^2}{3}$ parallel to the

axis of $x$ across this element from the negative to the positive side.

If this mutual action, or as it is generally called this *pressure*, when referred to unit of surface be denoted by the symbol $p$, we get the equation

$$p\,dy\,dz\,dt = \rho\,dy\,dz\,dt \cdot \frac{v^2}{3};$$

or

$$p = \rho\frac{v^2}{3} = \frac{\rho}{mh}.$$

Since the momenta parallel to $y$ and $z$ remain unaltered, it follows that the mutual action or pressure between portions of the medium separated by any plane is entirely normal to that plane.

Since also the expression for $p$, or $\rho\frac{v^2}{3}$, is independent of the direction of the axis of $x$, it follows that the pressure at any point of the medium is the same in all directions.

If we suppose the contiguous portions of the medium to be separated by a material instead of an ideal plane, it will clearly be necessary for the maintenance of the equilibrium that there should be an action between this plane and the adjacent portion of the medium exactly equivalent to the transference of momenta estimated above. Hence the pressure or force between the plane and medium is normal to the plane, and its value per unit of time and surface is $\frac{\rho}{mh}$ at any point. And this value remains unaffected by turning the plane of separation in any direction about the point.*

* It is important to distinguish between the velocity of agitation of the molecules treated of in the preceding reasoning and that which we are accustomed to consider as the velocity of the medium itself. This latter velocity has been defined by Professor Clerk Maxwell as follows. If we determine the motion of the centre of gravity of all the molecules within a very small region surrounding a point in a medium, then the velocity of the medium within that region is defined as the velocity of the centre of gravity of all the molecules within that region. Should such a velocity exist in the medium under consideration we must suppose that our ideal plane of separation moves with the same velocity, and therefore that the number of molecules crossing it in any direction is on the average equal to the number crossing it in the exactly opposite direction.

We may also prove that the values which we have found for $p$ and $\rho$ are sufficient for the equilibrium of the medium.

For consider the elementary parallelopiped $dx\,dy\,dz$ situated in the neighbourhood of the point $x, y, z$.

The positive momentum of the $N$ sphere matter within this element parallel to the axis of $x$ is, as we have seen, increased by the quantity $p\,dy\,dz\,dt$ in the time $dt$ by transference of matter across the face $dy\,dz$ nearer to the plane of $yz$, and the same momentum is, in the same time, diminished by the quantity $\left(p + \frac{dp}{dx}dx\right) dy\,dz\,dt$ by transference across the opposite face $dy\,dz$. On the whole, therefore, the positive momentum parallel to $x$ of the $N$ sphere matter within the element is diminished by the quantity $\frac{dp}{dx}dx\,dy\,dz\,dt$ in the time $dt$.

It is therefore necessary for the permanence of the state of the medium that the impressed force on the $N$ sphere matter within the element should produce a resultant momentum equal to the last found quantity in the time $dt$, in other words,

$$\frac{dp}{dx}dx\,dy\,dz\,dt \quad \text{should be equal to} \quad \rho X\,dx\,dy\,dz\,dt\,;$$

where $X$ is the impressed force at the point $x, y, z$ parallel to the axis of $x$; that is to say,

$$\frac{dp}{dx} \quad \text{should be equal to} \quad \rho X.$$

Now $$p = \frac{1}{mh}\rho, \quad \text{and} \quad \rho = mBe^{-hX};$$

$$\therefore \quad \frac{dp}{dx} = \frac{1}{mh}\frac{d\rho}{dx}, \quad \text{and} \quad \frac{d\rho}{dx} = -h\rho\frac{dX}{dx} = h\rho mX;$$

$$\therefore \quad \frac{dp}{dx} = \rho X,$$

the required equation.

When several different sets of spheres are present together in the region under consideration the distribution of the centres and of the velocities of the spheres of each set is, as we have seen, independent of the coexistence of the remaining sets. If

therefore $\rho_1$, $\rho_2$, &c. be the densities of the matter of the different sets in the neighbourhood of the point $x$, $y$, $z$, and if $p_1, p_2$, &c. be the pressures at that point, defined as above, of the media composed of these different sets, and if $m_1$, $m_2$, &c. be the masses of the individual spheres of each of the sets, and $p$ the total pressure, we shall have

$$p = p_1 + p_2 + \&c.$$

$$= \frac{\rho_1}{m_1 h} + \frac{\rho_2}{m_2 h} + \&c.$$

We will now summarise the results at which we have arrived concerning the physical properties of a medium of sets of elastic spheres moving about in a region of space very much larger than the sum of the volumes of the spheres, and acted on by any impressed forces tending to fixed centres.

In the first place we have found that there is one physical property which has the same value for every set, namely, the mean vis viva of each of the spheres, or $\frac{3}{2h}$. Let us call this quantity $\tau$.

In the second place we have found that the distribution of the positions and velocities of each set of spheres is independent of the remaining sets, and is in all respects the same as if that particular set alone existed in the region of space under consideration.

In the third place we have found that $p$, the pressure at any point referred to unit of surface, between contiguous portions of the medium arising from the action of any one of the sets is equal to $\frac{2}{3m}\rho\tau$, where $\rho$ is the density of the matter of that particular set in the neighbourhood of the point considered, and $m$ is the mass of each of the spheres of that set, $\tau$ being defined as above, and we have also proved that if $X$, $Y$, and $Z$ be the component forces at that point, then

$$\frac{dp}{dx} = \rho X, \qquad \frac{dp}{dy} = \rho Y, \qquad \frac{dp}{dz} = \rho Z.$$

In the fourth place we observe that the fraction $\frac{\rho}{m}$ represents

the number of spheres of the set under consideration per unit of volume in the neighbourhood of the point considered. It follows therefore from the equation $p = \frac{2}{3m} \cdot \rho\tau$ that whenever two media composed of different sets of spheres are so related that the pressure at any point and the mean vis viva of any one sphere are the same in each medium, then the number of spheres, per unit of volume, is also the same in each medium, or what is the same thing, that the densities of the matter of the two media are in such a case proportional to the masses of the individual spheres.

Comparing these results with the well-known properties of a mixture of gases in equilibrium, we know in the first place that there is one physical property, namely the temperature, which is constant throughout such a mixture.

In the second place it has long been recognised as a law established by Dalton that in such a mixture the density of each of the gases at any point is the same as if the other gases did not exist, or, as it is frequently expressed, each gas acts as a vacuum to all the rest.

In the third place we know from Boyle's law that so long as the temperature remains the same, the pressure is proportional to the density or inversely proportional to the volume.

In the fourth place we know from the law established by Dalton, Gay Lussac, and Charles, that when the temperature and density both vary, the pressure varies as the temperature and density conjointly.

Finally, we know from Gay Lussac's law that when two gases are at the same pressure and temperature the number of atoms in unit volume are the same.

We see therefore that in these four particulars the physical properties of a perfect gas, or of a mixture of such gases, exactly correspond with the physical properties of a medium consisting of a set of elastic spheres, or of a mixture of sets of such spheres when the mean vis viva of a sphere is taken as representing the temperature of the gases, or mixture of gases, and the sphere represents the chemical atom.

Up to this point therefore we have a very strong presump-

tion that the constitution of a homogeneous perfect gas may be explained by supposing it to be a collection of elastic spheres, equal to each other in all respects, and comprised in a region whose volume is very much larger than the sum of the spheres, the temperature of the gas being measured by the mean vis viva of any one of the spheres.

There are however other well-known properties of gases which are not adequately explained on this hypothesis of elastic spheres, the most important of which is the numerical value of the ratio of the specific heats at constant volume and constant pressure respectively.

The quantity of heat required to raise the temperature of unit of mass of any substance one degree is called the specific heat of that substance. In the case of gases this quantity is greater when the gas is allowed to expand under constant pressure than when the volume is kept constant, as when the gas is confined in a rigid vessel, the physical reason of the difference being that in the former case part of the applied heat is converted into mechanical work.

The ratio of the specific heat at constant pressure to that at constant volume has an important bearing on the theory of sound, and has been determined for many gases by careful experiment.

The value of this ratio for several of the more permanent gases, as hydrogen, oxygen, nitrogen, atmospheric air, carbonic oxide, nitrous oxide, and hydrochloric acid, is nearly 1·408; that of the more easily liquifiable gases, as chlorine, ammonia, and sulphuretted hydrogen, is about 1·3; and that of carbonic acid, nitric oxide, sulphurous acid, and marsh gas is about 1·26.

On the hypothesis of smooth elastic spheres this ratio ought to be exactly $1\cdot\frac{2}{3}$ or 1·6, as may be seen from the following reasoning:—Suppose $r$ to be the number of such spheres in a unit of mass of the medium, $v$ the volume occupied by such unit, and $m$ the mass of each sphere, then we have the equations

$$mr = 1, \quad \text{and} \quad \rho v = 1.$$

Also if $\tau$ be the mean vis viva, corresponding to the temperature of the gas, and $p$ the pressure referred to unit of surface,

$$pv = \tfrac{2}{3} r\tau.$$

Let the mechanical energy $\delta Q$ in the shape of heat when applied to the medium increase the mean vis viva from $\tau$ to $\tau+\delta\tau$, the volume remaining constant, then we must have the equation

$$\delta Q = r\delta\tau.$$

Next let the volume be allowed to vary so that the pressure remains constant, and let $\delta' Q$ be the mechanical energy required to raise the mean vis viva from $\tau$ to $\tau+\delta\tau$ in this case.

Since the mass expands under the pressure $p$, external work equal to $p\delta v$ is performed, $\delta v$ being the increase of volume, and therefore by the law of conservation of energy

$$\delta' Q = r\delta\tau + p\delta v.$$

But $pv = \frac{2}{3}r\tau$, and $p$ is constant;

$$\therefore \quad p\delta v = \tfrac{2}{3}r\delta\tau;$$

$$\therefore \quad \frac{\delta' Q}{\delta Q} = \frac{1+\frac{2}{3}}{1} = 1.\dot{6}.$$

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The only gas for which the ratio has so large a value as this is mercury gas, for which MM. Kundt and Warburg find it to be 1·67.* It is remarkable that the molecule of this substance is regarded by most chemists as monatomic.

There are also other phenomena exhibited by heated gas which suggest a somewhat less simple constitution of the medium than that of moving elastic spheres.

It is known that the light emitted by heated gas, so long as the gas is of no great density, consists of rays of one or more definite kinds of refrangibility, so that when this light is examined by the spectroscope, the spectrum produced consists of one or more bright lines, narrow and distinct, the intervening spaces being dark. As the density of the gas increases, these bright lines become broader and the intervening spaces more luminous, until, as the gas becomes very much condensed, a continuous spectrum is produced.

If now we replace the moving spheres of the foregoing propositions by a number of bodies all similarly constituted, made up of parts capable of relative motion without being

* See 'Nature' for October, 1875.

altogether torn asunder, this relative motion will be some kind of vibration. The motion of translation or agitation of these small bodies, or *molecules*, is, as we have seen in the case of the spheres, exceedingly irregular, the intervals between successive encounters and the velocities of a molecule during successive free paths not being subject to any law. It will be different however with the internal motions or vibrations of each molecule. When there is a long free path very many such vibrations may take place in the interval between successive encounters. At each encounter the whole molecule is roughly shaken. During the free path it vibrates according to its own laws, and these vibrations, as is the case in every connected system, may be resolved into a number of simple vibrations, the law of each of which is that of the simple pendulum. At any instant the number of molecules in collision is negligible in comparison with the whole number of molecules in the region under consideration. And therefore at any instant we have a collection of a very great number of bodies, all of which may be regarded as performing precisely the same set of vibrations. If these molecules be capable of communicating their vibrations to the luminiferous ether, the result will be light of one or more definite kinds of refrangibility, provided there be any light at all—that is, provided that the vibrations be of such a period as to belong to the luminous part of the spectrum. As the density of this medium is increased, the length of the free path of each molecule is diminished, and since each fresh encounter disturbs the regularity of the series of vibrations, we must no longer regard the whole of the bodies or molecules, but only a large majority of them at any instant, as performing the same sets of vibrations; the result therefore will be light of one or more definite kinds of refrangibility, with a mixture of fainter light of no definite refrangibility, or, viewed under the spectroscope, bright lines of light, along with a ground of diffused light forming a continuous spectrum.*

Let us now proceed to the reconsideration of the problem of the last proposition, the sets of smooth spheres being replaced

* See Maxwell, 'Theory of Heat,' p. 306.

by sets of exactly similar *molecules*—that is to say, bodies made up of parts which are capable of relative motion without being torn asunder.

The simplest conception of such bodies would be to regard them as composed of discrete atoms acting upon each other with forces any functions of the distance between them, and in this way the problem has been treated by Dr. Ludwig Boltzmann in his memoirs 'Über das Wärmegleichgewicht zwischen mehratomigen Gasmolekülen,' published in the Transactions of the Imperial Philosophical Academy of Vienna.* For the sake of somewhat greater generality we shall regard our molecules as bodies capable of a given number of degrees of freedom, in other words determined both as to position and arrangement of parts by a given number of generalised coordinates.

These molecules may be acted on by forces either internal, i.e. arising from the mutual action of the different parts of the same system, or external, and directed to fixed centres, but, *in a general way*, each molecule is conceived as being free from the action of any other molecule.

When the distance between any two molecules is so small that they are capable of exerting sensible forces upon one another there will be said to be an *encounter* between them, such encounters taking the place of the collisions in the case of the spheres, with this difference, that the time of an encounter will not be necessarily indefinitely small. We shall also consider that the forces acting upon the molecules are such that their components may be expressed as the differential coefficients of some function with respect to displacements parallel to the axes of reference, and that they admit therefore of generalised components in terms of the generalised coordinates as explained in Thomson and Tait's 'Natural Philosophy,' vol. i. p. 219. With this explanation we proceed to the consideration of the following proposition.

* Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Mathematisch-Naturwissenschaftliche Classe, lxiii Band, Zweite Abtheilung, vii Sitzung von 9 März, 1871.

## PROPOSITION VII.

A number of sets of molecules, the molecules in each set being very numerous and exactly like each other, are in motion in a region of space which is very much larger than the sum of the volumes of all the contained molecules, and are acted on by given forces tending to fixed centres and functions of their distances from these centres, required the law of permanent distribution of coordinates and momenta.

Let the number of generalised coordinates of each of the molecules of one of the given sets be $m$, and let them be denoted by the symbols $p_1$, $p_2$, &c., $p_m$. Let the corresponding momenta be also denoted by the symbols $q_1$, $q_2$, &c., $q_m$.

Let the total number of molecules of this set be $M$, and let $dM$ of these be in the state $A$ at any time—that is, let them have their coordinates and momenta intermediate between the values $p_1$ and $p_1 + dp_1$, &c., $p_m$ and $p_m + dp_m$, $q_1$ and $q_1 + dq_1$, &c., $q_m$ and $q_m + dq_m$.

Let also $$dM = f_m(p_1 \cdots p_m, q_1 \cdots q_m)\, dp_1 \ldots dq_m.$$

It is required to find the form of $f_m$ in order that it may remain the same for all time.

If $\phi_1 = a_1$, $\phi_2 = a_2$, &c. be any equations obtained by the elimination of $t$ from the integrals of any of the $2m$ equations of motion of one of the $M$ set of molecules, then by reasoning in all respects the same as that employed in Proposition IV it may be proved that so long as there are no encounters the condition of permanent distribution will be satisfied, provided $f_m$ be of the form

$$f_m(\phi_1, \phi_2, \text{&c.}).$$

It remains to find what further restriction must be imposed upon the form of $f_m$ in order that this permanence of arrangement may not be disturbed by any possible encounters.

Suppose that there is another set of $N$ molecules, each of which has $n$ generalised coordinates $r_1$, $r_2$, &c., $r_n$, with the corresponding generalised momenta $s_1$, $s_2$, &c., $s_n$, and let $dN$ of these be in the state $B$ at any time, that is let them have their coordinates and momenta intermediate between $r_1$ and

$r_1+dr_1$, &c., $r_n$ and $r_n+dr_n$, $s_1$ and $s_1+ds_1$, &c., $s_n$ and $s_n+ds_n$, and suppose that

$$dN = f_n(r_1 \ldots r_n\, s_1 \ldots s_n)\, dr_1 \ldots dr_n\, ds_1 \ldots ds_n.$$

Therefore the number of pairs of molecules consisting of one molecule of the set $M$ in state $A$ and another molecule of the set $N$ in state $B$ at any time must be

$$f_m(p_1 \ldots p_m q_1 \ldots q_m) f_n(r_1 \ldots r_n s_1 \ldots s_n)\, dp_1 \ldots ds_n.$$

Let $\phi(p_2, \ldots p_m\, r_1 \ldots r_n)$ be such a function of the $m+n-1$ coordinates $p_2 \ldots p_m$, $r_1 \ldots r_n$ that whenever $p_1$ differs from $\phi_1$ by less than a certain value $a$, that is whenever the quantity $x$ in the equation

$$p_1 - \phi = x \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

is equal to or less than $a$, there is an encounter between the corresponding molecules of the $M$ and $N$ set.

Eliminate $p_1$ and $dp_1$ by means of equation (1), and the last found expression becomes

$$f_m(p_1 \ldots p_m\, q_1 \cdot q_m) f_n(r_1 \ldots r_n\, s_1 \ldots s_n)\, dx\, dp_2 \ldots dq_m\, dr_1 \ldots ds_n, \ldots (2)$$

$p_1$ being expressed in terms of $x$ and the other variables by means of equation (1). The expression (2) gives the number of pairs of molecules, whereof one is in the state $A$ and the other in the state $B$ at any time: we call such pairs $(AB)$ pairs of molecules.

Let us now introduce the following restriction in the definition of our $AB$ pairs of molecules, namely, that while the values of the $2(m+n)-1$ variables $p_2 \ldots s_n$ defining the state of the pair remain as before, the value of the remaining variable $p_1$ is such as to make $x$ equal to $a$; and let us also take $dx$ equal to $\frac{dx}{dt}\delta t$, where $\frac{dx}{dt}$ is formed by the total differentiation of $x$, or $(p_1-\phi)$ with respect to $t$, when the variables in $p_1-\phi$ have been expressed in terms of $t$ by means of the equations of motion of the molecules. Then it is clear, by reasoning precisely the same as that employed in the elastic spheres, that every one of the $(AB)$ pair of molecules will commence an encounter in the time $\delta t$, or in other words the expression

$$f_m \cdot f_n \cdot dp_2 \ldots dq_m \cdot dr_1 \ldots ds_n \frac{dx}{dt} \cdot \delta t$$

will give us the number of encounters in time $\delta t$ between a pair

of molecules in the $AB$ state, i. e. with variables intermediate between $p_2$ and $p_2+dp_2 \dots s_n$ and $s_n+ds_n$, $p_1$ being made equal to $\phi+a$ in $f_m$ and $\frac{dx}{dt}$ being found as above explained.

At the end of the time $t+\tau$ let the value of $x$ become again equal to $a$, i.e. let the encounter terminate, and let the values of $p_2 \dots q_m$, $r_1 \dots s_n$ at the same instant be $P_2 \dots Q_m$, $R_1 \dots S_n$.

Then every encounter between a pair of molecules of the $M$ and $N$ set commencing with the variables $p_2 \dots s_n$ being situated within the limits $p_2$, and $p_2+dp_2$, &c., &c., $s_n$ and $s_n+ds_n$, i.e. in the $(AB)$ state, will terminate after an interval $\tau$ with the same variables being situated within the limits $P_2$ and $P_2+dP_2$, &c., &c., $S_n$ and $S_n+dS_n$, i.e. in the $(A'B')$ state.

Conversely, every encounter commencing between pairs of molecules in the $(A'B')$ state, with the exception only that their momenta have opposite signs to the corresponding momenta in that state, must terminate after the same interval $\tau$ in the $(AB)$ state.

It will follow therefore that in order that the permanence of the distribution of the medium may not be affected by an $(AB)$ encounter, the number of such encounters commencing in the time $\delta t$ must be equal to the number of $(A'B')$ encounters commencing in the same time. But by giving suitable values to the variables $p_2 \dots s_n$, all possible encounters between a molecule of the $M$ set and another of the $N$ set may be represented by an $AB$ encounter, and therefore in order that the permanence of the distribution of the medium may not be affected by any encounter between an $M$ and $N$ molecule the above-mentioned condition must be filfilled.*

Now we have seen that the number of $(AB)$ encounters commencing in the time $\delta t$ is equal to

$$f_m(p_1 \dots q_m)\, f_n(r_1 \dots s_n)\, dp_2 \dots ds_n \frac{dx}{dt} \cdot \delta t,$$

when we have substituted $\phi+x$ for $p_1$ and made $x$ equal to $a$.

* It is assumed, as self-evident, from our supposed constitution of the medium, that the number of pairs of spheres in the $A'B'$ state is the same as the number in that state with the signs of the momenta reversed.

Similarly the number of $A'B'$ encounters is

$$f_m(P_1,\ldots Q_m)\, f_n(R_1\ldots S_n)\, dP_2\ldots dS_n \frac{dX}{dt}\,.\,\delta t,$$

when we have substituted $\Phi + X$ for $P_1$ and made $X = a$.

Hence we must have

$$f_m(p_1\ldots q_m)\, f_n(r_1\ldots s_n)\, dp_2\ldots ds_n \frac{dx}{dt}$$

$$= f_m(P_1\ldots Q_m)\, f_n(R_1\ldots S_n)\, dP_2\ldots dS_n \frac{dX}{dt}\,.$$

Now $$dx\, dp_2\ldots ds_n = dp_1\, dp_2\ldots ds_n.$$

Also by the general proposition proved above

$$dp_1\, dp_2\ldots ds_n = dP_1\ldots dP_2\ldots dS_n\,;$$

and as before

$$dP_1\, dP_2\ldots dS_n = dX\, dP_2\ldots dS_n\,;$$

$$\therefore \quad dx\, dp_2\ldots ds_n = dX\, dP_2\ldots dS_n.$$

This last equation being true throughout the whole motion it follows that

$$dp_2\ldots ds_n \frac{dx}{dt} = dP_2\ldots dS_n \frac{dX}{dt},$$

and therefore that

$$f_m(p_1\ldots q_m)\, f_n(r_1\ldots s_n) = f_m(P_1\ldots Q_m)\, f_n(R_1\ldots S_n).$$

We have seen that $f_m$ and $f_n$ must be of the forms $f_m(\phi_1, \phi_2, \text{\&c.})$, and $f_n(\psi_1, \psi_2, \text{\&c.})$ where $\phi_1 = a_1$, $\phi_2 = a_2$, &c. are equations found by eliminating $t$ from any of the integrals of the $2m$ equations of motion of one of the $M$ set of molecules and $a_1$, $a_2$, &c., are arbitrary constants, while $\psi_1$, $\psi_2$ are similarly related to the equations of motion of one of the $n$ set of molecules.

And therefore the equation of condition found above becomes

$$f_m(\phi_1, \phi_2, \text{\&c.})\, f_n(\psi_1, \psi_2, \text{\&c.}) = f_m(\Phi_1, \Phi_2, \text{\&c.})\, f_n(\Psi_1, \Psi_2, \text{\&c.})$$

Of all the equations of the form $\phi = a$ and $\psi = b$ let us take the equations of conservation of energy and those only, so that $f_m$ and $f_n$ become $f_m(\phi)$ and $f_n(\psi)$ where $\phi$ and $\psi$ are the sum of the potential and kinetic energies of the respective molecules; then since the total energy, kinetic and potential, in any pair

of molecules must be the same before and after an encounter our equation becomes

$$f_m(\phi) f_n(\psi) = f_m(\Phi) f_n(\Psi),$$

subject to the condition

$$\phi + \psi = \Phi + \Psi.$$

Hence, as in the first proposition, we conclude that

$$f_m(\phi) = Ae^{-h\phi} \quad \text{and} \quad f_n(\psi) = Be^{-h\psi};$$

and the expression for $dM$, or the number of molecules of the $M$ set in the state $(A)$ at any time $t$, becomes

$$Ae^{-h(\chi+T)} dp_1 \ldots dp_m \, dq_1 \ldots dq_m,$$

where $\chi$ is the potential and $T$ the kinetic energy corresponding to the state $(A)$ of a molecule. It is obvious that the same law may by the same reasoning be shewn to ensure the permanence of distribution as far as encounters between a pair of molecules from any other pair of sets, or from any similar set, is concerned: it is therefore the law of distribution which we require.

The constant $h$ is the same for every set of molecules, but $A$ may be different for different sets. Hence we see, in the first place, that the law of the arrangement of any one set of molecules is the same as if that set existed alone in the region of space under consideration.

Let the three coordinates $p_1$, $p_2$, $p_3$ be the three rectangular coordinates of the centre of mass of the molecule, and let them be denoted by $x$, $y$, $z$, then if $\mathrm{m}$ be the mass of the molecule, and $u$, $v$, $w$ be the component velocities of its centre of mass parallel to the same axes, the values of $q_1$, $q_2$, and $q_3$ will become $\mathrm{m}u$, $\mathrm{m}v$, and $\mathrm{m}w$, so that if $p_4$, $p_5$, &c.... $p_m$ be the generalised coordinates of the molecule relative to its centre of mass, and $q_4$, $q_5$, ... $q_m$ the corresponding momenta, the value of $T$ will become

$$\frac{\mathrm{m}}{2}(u^2 + v^2 + w^2) + f(p_4 \ldots p_m \, q_4 \ldots q_m),$$

where $f$ is the kinetic energy of the molecule relative to its centre of mass, and is therefore an essentially positive quadratic function of the $q$'s of the form

$$Q_4 q_4^2 + Q_5 q_5^2 + \&c. + R q_4 q_5 + \&c.,$$

the $Q$'s and $R$'s being known functions of the $p$'s.

Therefore the expression for $dM$, or the number of molecules of the $M$ set in the state $A$, takes the form of

$$Ce^{-h(\chi+f)}dx\,dy\,dz\,dp_4\ldots dp_m\,dq_4\ldots dq_m\,e^{-h\frac{m}{2}(u^2+v^2+w^2)}du\,dv\,dw.$$

If we integrate this with respect to all the independent variables except $u$, $v$, and $w$, we find that the number of molecules of the $M$ set, the component velocities of whose centres of mass parallel to the axes lie between $u$ and $u+du$, $v$ and $v+dv$, $w$ and $w+dw$, is equal to

$$De^{-h\frac{m}{2}\cdot c^2}du\,dv\,dw,$$

where $c^2 = u^2+v^2+w^2$ and $D$ is independent of $u$, $v$, and $w$.

From this result we infer, precisely as in the case of the elastic spheres,

(1°) That all directions of motion of the centres of mass of the molecules are equally probable.

(2°) That the mean velocity of agitation of a molecule is $\frac{2^{\frac{3}{2}}\cdot\sqrt{\pi}}{\sqrt{mh}}$.

(3°) „ square of the velocity of agitation is $\frac{3}{mh}$.

(4°) „ kinetic energy of agitations parallel to either axis is . . . . . $\frac{1}{2h}$.

(5°) „ kinetic energy of agitation is . . $\frac{3}{2h}$.

## PROPOSITION VIII.

A number of sets of molecules are in motion in a given region of space, under the circumstances of the last proposition, to find the action of one part of the medium upon another.

The reasoning in this case is in all respects identical with that employed in the corresponding proposition concerning the sets of elastic spheres, and hence we infer

(1) That the pressure or action between two portions of the medium separated by any plane is normal to that plane.

(2) That it is the same for all directions of the normal to that plane.

(3) That the amount of pressure, arising from any one set of molecules, referred to unit of surface is $\frac{\rho \overline{v^2}}{3}$ where $\rho$ is the density of the matter of which that particular set is composed in the neighbourhood of the point in question, and $\overline{v^2}$ is the mean square of their velocity of translation.

Therefore $p$, or the pressure referred to unit of surface arising from the action of any one set, is $\frac{\rho}{\mathrm{m}h}$, and the total value of $p$ is $\Sigma \frac{\rho}{\mathrm{m}} \cdot \frac{1}{h}$, where $\Sigma \frac{\rho}{\mathrm{m}}$ is the sum of the values of $\frac{\rho}{\mathrm{m}}$ for all the sets of molecules.

To find the value of $\rho$ for any one set of molecules in the neighbourhood of any point, we have for the number of molecules of the $M$ set in the state $A$ the expression

$$Ae^{-h(\chi+f)+\frac{\mathrm{m}}{2}(u^2+v^2+w^2)}dx\,dy\,dz\,du\,dv\,dw\,dp_4 \ldots dp_m\,dq_4 \ldots dq_m,$$

where $f$ is a function of the $p$'s and $q$'s as already explained.

Integrating with respect to all the momenta the result becomes

$$P.e^{-h\chi}.dx\,dy\,dz\,dp_4 \ldots dp_m,$$

where $P$ is a function of the $p$'s only.

Now the forces acting on the molecule are either mutual forces, if any, between different atoms of the molecule or forces tending to fixed centres without the molecule, and we conceive that the dimensions of the molecule are so very small in comparison with the distances of these centres from any parts of it that the latter forces are sensibly parallel and constant. It follows therefore that $\chi$, or the potential energy of the molecule, is the sum of two parts, viz. $\chi_1$, or the potential energy of the whole mass collected at the centre of mass and acted on by the external forces, and therefore a function of $x$, $y$, $z$ only, and $\chi_2$ or the potential energy of the mutual forces (if any), and therefore a function of the $p$'s only.

Therefore the number of molecules of the $M$ set, whose coordinates lie between $x$ and $x+dx$, &c. ... $p_m$ and $p_m+dp_m$, is

$$Pe^{-h(\chi_1+\chi_2)}dx\,dy\,dz\,dp_4\ldots dp_m,$$

where $P$ and $\chi_2$ are functions of the $p$'s only and $\chi_1$ is a function of $x$, $y$, $z$ only.

If therefore we integrate the last expression with respect to the $p$'s we find for the number of molecules of the $M$ set whose centres of mass lie within the parallelopiped $dx\,dy\,dz$ the expression

$$Ce^{-h\chi_1}dx\,dy\,dz,$$

So that $\rho = \mathrm{m}\,Ce^{-h\chi_1}$ and therefore, as in the elastic sphere case, we obtain the equations

$$\frac{dp}{dx}=\rho X, \qquad \frac{dp}{dy}=\rho Y, \qquad \frac{dp}{dz}=\rho Z.$$

From the results of this proposition we see, as in the elastic spheres, the agreement between the physical properties of a medium composed of sets of molecules such as we are now considering and a mixture of gases the temperature of which is taken equal to the mean kinetic energy of translation of any one of the molecules. (See pp. 22, 23 above.)

## PROPOSITION IX.

A number of sets of molecules are in motion in a given region of space under the circumstances of the two preceding propositions; required to find the mean value of the total kinetic energy of any molecule.

For a molecule of the $M$ set we have seen that the total kinetic energy $T$ is expressed by the equation

$$T=\frac{\mathrm{m}}{2}(u^2+v^2+w^2)+f,$$

where $f$ is equal to $Q_4q^2_4+Q_5q^2_5+$ &c. $+Rq_4q_5+$ &c. as explained above, and we have already proved that the mean value of the first term in the expression for $T$ is $\frac{3}{2h}$, we proceed now

to prove that the mean value of $f$ is $\frac{m-3}{2h}$, and therefore that the mean value of $T$ is $\frac{m}{2h}$.

Introduce $m-3$ new variables $r_4, r_5 \ldots r_m$ connected with the variables $q_4, q_5 \ldots q_m$ by the $m-3$ linear equations

$$\left.\begin{aligned} q_4 &= \lambda_4 r_4 + \lambda_5 r_5 + \&c. + \lambda_m r_m, \\ q_5 &= \mu_4 r_4 + \mu_5 r_5 + \&c. + \mu_m r_m, \\ &\&c., \qquad\qquad \&c. \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots (a)$$

The $\lambda$'s and $\mu$'s being like the $Q$'s and $R$'s functions of the $m-3$ coordinates $p_4 \ldots p_m$.

Now (Salmon's 'Higher Algebra,' Lesson xii., p. 88) we may determine the $\lambda$ and $\mu$ coefficients in an infinite number of ways, so that the function $f$ may assume the form

$$r_4^2 + r_5^2 + \&c. + r_m^2,$$

the signs preceding each of the terms being positive because no possible values of the $q$'s, and therefore (by equations $a$) no possible values of the $r$'s can make $f$ negative.

Now since $dM$ is the number of molecules of the $M$ set in the state $A$, at any time it follows that the mean value of such a quantity as $r^2$ is equal to

$$\frac{\Sigma(r^2 dM)}{\Sigma(dM)}.$$

Eliminate the $q$'s from the expression for $dM$ found above, i.e.

$$Ae^{-h(\chi+T)}.\, dx \ldots dq_m,$$

by means of the equations ($a$), and it becomes

$$A\Delta e^{-h\chi}\, dx \ldots dp_m \,.\, e^{-\frac{mh}{2}(u^2+v^2+w^2)} du dv dw e^{-h(r_4^2+\&c.\ldots+r_m^2)} dr_4 \ldots dr_m,$$

where $\Delta$ is the functional determinant

$$\begin{vmatrix} \frac{dq_4}{dr_4} & \ldots\ldots & \frac{dq_4}{dr_m} \\ \frac{dq_m}{dr_4} & \ldots\ldots & \frac{dq_m}{dr_m} \end{vmatrix},$$

and therefore independent of the $r$'s, since the equations ($a$) are linear. Also, since each of the $q$'s ranges over all values from $-\infty$ to $+\infty$, it follows from the equations ($a$) that each of the $r$'s must admit of a corresponding range.

But $\int_{-\infty}^{\infty} e^{-hr^2} r^2\, dr$ is $\frac{\sqrt{\pi}}{2h^{\frac{3}{2}}}$, and $\int_{-\infty}^{\infty} e^{-hr^2} dr$ is $\frac{\sqrt{\pi}}{\sqrt{h}}$.

Therefore

$$\therefore\ \Sigma r^2\, dM = \frac{1}{2h}\left(\frac{\pi}{h}\right)^{\frac{m}{2}} A \iint \ldots \Delta e^{-h\left\{\chi + \frac{\mathrm{m}}{2}(u^2+v^2+w^2)\right\}} dx\, dy\, dz\, du\, dv\, dw;$$

$$\text{and}\quad \Sigma dM = \left(\frac{\pi}{h}\right)^{\frac{m}{2}} A \iint \ldots \Delta e^{-h\left\{\chi + \frac{\mathrm{m}}{2}(u^2+v^2+w^2)\right\}} dx\, dy\, dz\, du\, dv\, dw;$$

and therefore the quotient, or the mean value of $r^2$, is $\frac{1}{2h}$.

But the mean value of $f$ is $m-3$ times that of any one of the squares of $r$. Therefore the mean value of $f$ is $\frac{m-3}{2h}$ and the mean value of $T$ is $\frac{m}{2h}$.*

## PROPOSITION X.

A homogeneous gas being supposed to be constituted of moving molecules with any given number of degrees of freedom, required to find the ratio of the specific heat at constant pressure to that at constant volume.

First suppose that when a small quantity $\delta Q$ of heat is imparted to a unit of mass of the gas the temperature is raised from $\tau$ to $\tau + \delta\tau$, the volume remaining constant.

Since the volume remains unchanged there is no external work performed, and therefore the whole of this energy $\delta Q$ must be accounted for by increase of the total kinetic energy and of the potential energy, therefore

$$\delta Q = r(\delta\tau + \delta\chi),$$

where $\delta\tau$ and $\delta\chi$ are the increases of mean total kinetic and

* The result in the text may also be arrived at by direct integration of the expressions

$$\int\int \ldots A e^{-h(\chi+T)}\, dx \ldots dq_m$$

and

$$\int\int \ldots A T e^{-h(\chi+T)}\, dx \ldots dq_m$$

over all values of the $q$'s, where $T$ is an essentially positive homogeneous and quadratic function of these variables.

potential energy respectively of any molecule, and $r$ is the number of molecules in the unit of mass.

We have proved that $T$, the mean total kinetic energy of a molecule, is equal to $\frac{m\tau}{3}$ where $m$ is the number of degrees of freedom of the molecule;

$$\therefore \quad \delta Q = r\left(\frac{m}{3} + \frac{d\chi}{dt}\right)\delta\tau.$$

Next let the volume be allowed to increase so that the pressure remains constant, and let $\delta' Q$ be the heat required to raise the unit of mass from $\tau$ to $\tau + \delta\tau$ in this case.

Since external work is performed equal to $p\,\delta v$ we must have in this case

$$\delta' Q = r\left(\frac{m}{3} + \frac{d\chi}{dt}\right)\delta\tau + p\,\delta v.$$

But we know that $pv = \frac{2r}{3}\cdot\tau$, and since $p$ remains constant it follows that $p\,\delta v = \frac{2r}{3}\delta\tau$;

$$\therefore \quad \frac{\delta' Q}{\delta Q} = \frac{m + 3\frac{d\chi}{dt} + 2}{m + 3\frac{d\chi}{dt}}.$$

All that we know of $\frac{d\chi}{dt}$ is that it must necessarily be positive, and of $m$ that it must be integral and not less than 3; writing therefore $e$ for $3\frac{d\chi}{dt}$ in the calculated value of the ratio of the specific heats, this becomes

$$\frac{m+e+2}{m+e},$$

or

$$1 + \frac{2}{m+e}.$$

We have seen that there is one gas for which the ratio is $1\frac{2}{3}$, giving us therefore $m+e = 3$, and thus agreeing with the case of the elastic spheres where there are three degrees of freedom

determined by the coordinates of the centre, and where there is no motion relative to the centre, so that $m = 3$ and $e = 0$.

For the majority of observed gases, however, the ratio is 1·408, giving us

$$\frac{2}{m+e} = \cdot 408,$$

and

$$m+e = 4\cdot 9.$$

For a few gases the ratio is 1·3, whence we get

$$\frac{2}{m+3} = \cdot 3,$$

and

$$m+e = 6\cdot 6.$$

And for a few other gases the ratio falls as low as 1·26, giving us

$$m+e = 8 \text{ nearly.}$$

The great difficulty in the establishment of the kinetic theory of gases on the molecular hypothesis is to conceive a material system so constituted as to give a suitable value for $m$ in the cases we have mentioned, especially for that most general case of all in which $m+e = 4\cdot 9$.

Hitherto we have supposed that the gas is so rare, or what is the same thing, that the free path of the molecule is so long, that the number of molecules engaged in encounters at any instant may be neglected in comparison with the number of those which are moving free from such encounters.

On this hypothesis we have found that the number of molecules, each with $m$ generalised coordinates, in any state (A) at any time may be expressed by the formula

$$Ce^{-h(\chi+T)}\, dp_1 \ldots dp_m\, dq_1 \ldots dq_m,$$

where $T$ is the kinetic and $\chi$ the potential energy of a molecule whose coordinates and momenta are $p_1, p_2 \ldots p_m, q_1, q_2 \ldots q_m$ respectively, the forces considered in $\chi$ being either the mutual forces between different atoms of the molecule, or external forces tending to fixed centres, but not forces arising from the action of surrounding molecules.

Let us consider now a mass of gas, containing an infinitely

large number of molecules in thermal equilibrium, and suppose that there are $r$ molecules in each unit of mass of this gas.

The chance of any one of these $r$ molecules, as $M_1$, being in the state $A_1$ is as we have seen

$$Ce^{-h(\chi_1+T_1)}\,ds_1\,d\sigma_1,$$

where $ds_1$ and $d\sigma_1$ are written for the products $dp_1 \dots dp_m$, $dq_1 \dots dq_m$ respectively, and $\chi_1$ and $T_1$ are the values of $\chi$ and $T$ when the coordinates and momenta have the values $p_1 \dots p_m$, $q_1 \dots q_m$ respectively.

Since the total number of molecules in the whole gas is infinitely large, the chance of any one of them being in any particular state may be regarded as independent of the states of the other molecules, and therefore the chance of the $r$ molecules in unit of mass being at any time in the states $A_1$, $A_2 \dots A_r$ respectively must be

$$Ce^{-h(\chi+T)}\,ds_1 \dots ds_r\,d\sigma_1 \dots d\sigma_r,$$

where $\chi = \chi_1 + \chi_2 \dots + \chi_r$, or the total potential energy of the whole of the $r$ molecules, and $T = T_1 + T_2 \dots T_r$, or the total kinetic energy of the whole of the $r$ molecules in that particular arrangement of the coordinates and velocities.

In this formula, as we have said, intermolecular forces do not enter into the value of $\chi$.

Now it has been proved by Dr. Ludwig Boltzmann in a memoir published in the sixty-fourth volume of the Transactions of the Imperial Philosophical Academy of Vienna, above referred to, that the formula just now obtained will equally represent the chance of the above arrangement of the $r$ molecules even when intermolecular forces are taken into account.

In point of fact it is clear that if the $r$ molecules of our unit of mass were to continue free from encounters with any of the remaining molecules, then the above law would ensure a permanent distribution whether intermolecular forces were considered or not, for $\chi + T$ would remain constant, and also the product of the differentials $ds_1 \dots ds_r, d\sigma_1 \dots d\sigma_r$, by what has been proved on p. 12. In fact the reasoning would be in all respects the same as that employed in Prop. IV above, the whole $r$

molecules together taking the place of any one molecule in that proposition.

In the memoir referred to it is demonstrated that this law of distribution remains unaltered when the effect of encounters between other gas molecules in thermal equilibrium with the given mass of $r$ molecules is taken into consideration.

From this law of distribution it follows, by the same reasoning as has been already employed, that if the mean kinetic energy of agitation of a molecule be taken to represent the temperature $\tau$ of the gas, then the mean total kinetic energy of a molecule will be $\frac{m\tau}{3}$ ($m$ being the number of generalised coordinates of the molecule).

The value of $p$, or the pressure referred to unit of surface, will however no longer be equal to $\frac{\rho\overline{v^2}}{3}$, as it was in the case where the intermolecular forces were neglected, and before finding its corrected value it will be necessary to prove an important proposition due to Professor Clausius, premising the following definitions.

When any number of material particles are in motion within a limited space so that the particles do not remove continually further and further from their original positions, and provided also that the velocities of the particles do not continually increase or decrease, such a system of material particles is said to be in *stationary motion*.

If $X$, $Y$, $Z$ be the component forces upon any one of a system of particles in stationary motion, and $x$, $y$, and $z$ be the coordinates of such particle referred to any origin and axes, and the quantity $Xx+Yy+Zz$ be found for such particle, then the mean value of the expression

$$-\tfrac{1}{2}\Sigma(Xx+Yy+Zz)$$

during any period of stationary motion of the system, where $\Sigma$ represents summation for all the particles, is called the *Virial* of the system.

## PROPOSITION XI.

When a system of material particles is in stationary motion the mean vis viva of the system is equal to its virial.

If $x$ be any function of $t$,

$$\frac{d^2}{dt^2}(x^2) = 2\frac{d}{dt}\cdot\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2};$$

$$\therefore\ 2\left(\frac{dx}{dt}\right)^2 = -2x\frac{d^2x}{dt^2} + \frac{d^2}{dt^2}(x^2). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (a)$$

Let $x$ be the coordinate parallel to the axis of $x$ at the time $t$ of that one of the material particles whose mass is $\mathrm{m}$, and let $X$ be the component force on that particle parallel to the same axis, then

$$\mathrm{m}\frac{d^2x}{dt^2} = X.$$

Hence equation ($a$) gives us

$$\frac{\mathrm{m}}{2}\left(\frac{dx}{dt}\right)^2 = -\frac{Xx}{2} + \frac{\mathrm{m}}{4}\cdot\frac{d^2}{dt^2}(x^2),$$

$$\therefore\ \frac{\mathrm{m}}{2t}\cdot\int_0^t\left(\frac{dx}{dt}\right)^2 dt = -\frac{1}{2t}\cdot\int_0^t Xx\,dt + \frac{\mathrm{m}}{4t}\cdot\left[\frac{d(x^2)}{dt} - \left[\frac{d(x^2)}{dt}\right]_0\right],$$

where $\left[\frac{d(x^2)}{dt}\right]_0$ denotes the initial value of $\frac{d(x^2)}{dt}$.

Now $\frac{1}{t}\cdot\int_0^t\left(\frac{dx}{dt}\right)^2 dt$ and $\frac{1}{t}\cdot\int_0^t Xx\,dt$ are the mean values of $\left(\frac{dx}{dt}\right)^2$ and $Xx$ during the time $t$.

If the motion be strictly periodic and $t$ be taken equal to the length of a period or any multiple whatever of that length, then the last term on the right-hand side becomes zero; and if the motion be not strictly periodic, still from its stationary character as above defined, although the coefficient of $\frac{\mathrm{m}}{4t}$ in the last term does not necessarily become zero for any value of $t$ however large, yet its value cannot increase indefinitely, but can only fluctuate within certain limits, and therefore by sufficiently

increasing the value of $t$ the last term on the right-hand side becomes inappreciable and may be neglected, so that we obtain, in either case, the equation

$$\frac{\mathrm{m}}{2}\cdot\overline{\left(\frac{dx}{dt}\right)^2} = -\tfrac{1}{2}\overline{Xx};$$

and therefore by similar reasoning with respect to $y$ and $z$, $Y$ and $Z$,

$$\frac{\mathrm{m}}{2}\cdot\overline{\left[\left(\frac{dx}{dt}\right)^2+\left(\frac{dy}{dt}\right)^2+\left(\frac{dz}{dt}\right)^2\right]} = -\tfrac{1}{2}\overline{(Xx+Yy+Zz)},$$

or

$$\frac{\mathrm{m}}{2}\cdot\overline{v^2} = -\tfrac{1}{2}\overline{(Xx+Yy+Zz)};$$

and therefore for any system of particles,

$$\Sigma\frac{\mathrm{m}}{2}\overline{v^2} = -\tfrac{1}{2}.\Sigma\overline{(Xx+Yy+Zz)}.$$

If the force $X$, $Y$, $Z$ arise from the mutual actions of the particles, the expression for the virial may be modified as follows :—

Let $R$ be the force (supposed to be attractive) between any two particles $\mathrm{m}$ and $\mathrm{m}'$ whose coordinates are $xyz$, $x'y'z'$, and distance apart $r$.

Then

$$Xx+X'x' = R\frac{x'-x}{r}\cdot x + R\frac{x-x'}{r}x' = -R\frac{(x'-x)^2}{r},$$

with similar expressions for $Yy+Y'y'$, $Zz+Z'z'$;

$$\therefore\quad -\tfrac{1}{2}(Xx+X'x'+Yy+Y'y'+Zz+Z'z') = \tfrac{1}{2}Rr.$$

Extending this result to any number of particles we find

$$-\tfrac{1}{2}\Sigma(Xx+Yy+Zz) = \tfrac{1}{2}\Sigma Rr,$$

and

$$-\tfrac{1}{2}\Sigma\overline{(Xx+Yy+Zz)} = \tfrac{1}{2}\Sigma\overline{Rr},*$$

the bar indicating mean values.

* $\Sigma(\overline{Rr})$ represents the mean value of the sum $\Sigma(Rr)$ taken for all possible configurations.

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## PROPOSITION XII.

A number of material particles are in motion within a closed surface under the action of their mutual forces, required to find the pressure on the surface supposed to be normal to that surface and uniform throughout.

By the last proposition we have

$$\Sigma \frac{m}{2} \overline{v^2} = -\tfrac{1}{2} \Sigma (\overline{Xx + Yy + Zz}).$$

Also the part of the virial which depends upon mutual forces between the particles has been proved to be equal to

$$\tfrac{1}{2} \Sigma \overline{Rr},$$

where $R$ is the force (assumed attractive) and $r$ the distance between any two of the particles. It remains to determine that part of the virial which depends upon the normal pressure.

Let $p$ be this pressure referred to unit of surface, and let $\alpha$, $\beta$, $\gamma$ be the angles which the normal to the surface drawn inwards at any point makes with the axes, and let $r$ be the distance of that point from the origin.

Then the part of the virial arising from the pressure on the element $\delta S$ of the surface at this point will be

$$-\frac{p}{2} \delta S (x \cos\alpha + y \cos\beta + z \cos\gamma),$$

that is

$$-\frac{p}{2} \cdot r \delta S \cos\theta,$$

where $\theta$ is the angle between $r$ and the normal to the surface, drawn inwards.

Conceive a small conical surface to be described, having the origin of coordinates for its vertex, and for its base the element $\delta S$ of the surface.

If $\delta V$ be the volume of this elementary cone it is clear that $\frac{\delta S}{2} r \cos\theta$ will be equal in magnitude to $\frac{3}{2} \delta V$, and will be positive or negative according as $r$ meets the surface on the outside or the inside.

Taking the sum of these elementary cones it is clear that the

excess of the negative over the positive sum will be equal to the volume included within the surface.

Hence the whole virial becomes

$$\tfrac{1}{2}\overline{Rr}+\tfrac{3}{2}pV,$$

where $V$ is the volume within the surface, and therefore we have this equation for determining $p$,

$$pV=\tfrac{1}{3}\Sigma m\overline{v^2}-\tfrac{1}{3}\Sigma\overline{Rr}.$$

If the material particles be replaced by molecules it is easy to see that the above-proved property of the virial still holds, when $x$, $y$, and $z$ represent the coordinates of the centre of mass of the molecule, and $X$, $Y$, and $Z$ are the component forces acting on the molecule supposed to be applied at the centre of mass.

We shall therefore have the equation

$$\Sigma\frac{m}{2}\overline{v^2}=-\tfrac{1}{2}\Sigma(\overline{Xx+Yy+Zz})+\tfrac{3}{2}pV,$$

where the first term is the part of the virial arising from the mutual forces between the molecules.

It will not be rigorously true for two molecules of any form as it is for two material particles that

$$Xx+X'x'+Yy+Y'y'+Zz+Z'z'=-\tfrac{1}{2}Rr,$$

$R$ being the mutual force between the molecules (estimated as if the mass of each molecule were collected at its centre of mass), but inasmuch as for the large majority of pairs of molecules their distances apart are infinitely large as compared with their dimensions, and also, in taking the mean value of $Xx+Yy+Zz$, we have to include cases in which the molecules are presented to each other in all manner of relative directions, we conclude, as before, that the mean value of $Xx+Yy+Zz$ may be represented by the mean value of $-Rr$ calculated as if the molecules were material points, so that in all cases we have

$$pV=\tfrac{2}{3}r\tau-\tfrac{1}{3}\Sigma Rr,$$

where $\tau$ is the temperature, or the mean value of the kinetic energy of translation of a molecule.

When $R=0$, then $pV=\frac{2}{3}r\tau$, agreeing with the result already obtained for the cases in which there are no intermolecular actions.

## PROPOSITION XIII.

To deduce the second law of thermodynamics from the results of the kinetic theory of gases.

We have proved that if a gas be composed of an infinite number of molecules, as in the preceding propositions, the chance of any $r$ molecules being in the particular state $A$ at any time may be represented by

$$Ce^{-h(\chi+T)}ds_1 \ldots ds_r\, d\sigma_1 \ldots d\sigma_r,$$

where $\chi$ and $T$ are the total potential and kinetic energy of the $r$ molecules in the state $A$, and $ds_1$ &c. $\ldots$ $d\sigma_r$ have the meanings assigned to them on p. 40.

Let three of the generalised coordinates in the case of each molecule be the three coordinates of the centre of mass, viz. $x_1 y_1 z_1$ &c., $x_r y_r z_r$, then the above chance may be represented by

$$Ce^{-h(\chi+T)}.\, dx_1 \ldots dz_r .\, ds\, .\, d\sigma,$$

the $ds$ comprising the product of the differentials of all the coordinates except the $x$, $y$, and $z$'s, and the $d\sigma$ comprising the product of the differentials of all the momenta. Also $T$ is of the form $\Sigma \frac{m}{2}(u^2+v^2+w^2)+f$, where $f$ is a sum of quadratic functions of the momenta relative to the centres of mass of the different molecules.

Integrating with regard to the momenta, we see that the chance of any configuration may be represented by

$$Pe^{-h\chi}\, ds\, .\, dx_1 \ldots dz_r,$$

where $P$ is a function of all the $mr$ coordinates except the $3r$, $x$, $y$, and $z$'s, and $ds$ is the product of the differentials of these $(m-3).r$ coordinates.

Hence it follows that the mean value $\bar{f}$ of any function $f$ of the positions of the molecules will be determined by the equation

$$\bar{f} = \frac{\int\int\int \ldots f P e^{-h\chi} ds\, dx_1 \ldots dz_r}{\int\int\int \ldots P e^{-h\chi} ds\, dx_1 \ldots dz_r},$$

and that $\bar{\chi}$ or the mean value of the potential energy will be determined by the equation

$$\bar{\chi} = \frac{\int\int\int \ldots \chi P e^{-h\chi} ds\, dx_1 \ldots dz_r}{\int\int\int \ldots P e^{-h\chi} ds\, dx_1 \ldots dz_r}.$$

Suppose now that this unit of mass of gas, consisting of $r$ molecules, is contained in an envelope under the pressure $p$ referred to unit of surface, the volume enclosed by the envelope being $v$, and let a small accession of heat $\delta Q$ be imparted to it.

Then $h$ and $v$ will, in general, vary; let their increments be denoted by $\delta h$ and $\delta v$ respectively.

There will therefore be an increase of mean kinetic and mean potential energy, the former being $\delta\left(\frac{3r}{2h}\right)$ or $-\frac{3r}{2h^2}\delta h$, and the latter being $\delta\bar{\chi}$, where $\delta\bar{\chi}$ has to be determined by the methods given above.

There will also be external work produced equal to $p\delta v$, and therefore by the conservation of energy we must have

$$\delta Q = -\frac{3r}{2h^2}\delta h + \delta\bar{\chi} + p\delta v;$$

whence we get

$$\frac{\delta Q}{\tau} = -\frac{r}{h}\delta h + \frac{2h}{3}\delta\bar{\chi} + \frac{2h}{3}p\delta v.$$

And the second law of thermodynamics requires that $\frac{\delta Q}{\tau}$, and therefore $-\frac{r}{h}\delta h + \frac{2h}{3}\delta\bar{\chi} + \frac{2h}{3}p\delta v$, should be a perfect differential for all values of $\delta h$ and $\delta v$.

Let us in the first place suppose that there are no intermolecular forces, and let $u$ be taken equal to the expression

$$\log \int\int\int \ldots P e^{-h\chi} ds\, dx_1 \ldots dz_r.$$

Now $P$ and the differentials included in $ds$ are functions only of the coordinates relative to the centre of mass of the molecules, and are therefore independent of $v$.

Also since there are no intermolecular forces, it follows that $\chi$ is also independent of $v$.

Therefore $$\delta u = \frac{du}{dh}\delta h + \frac{du}{dv}\delta v,$$

where the latter term on the right-hand side represents the increase of $u$ arising from the variation of the limits of integration consequent upon the expansion.

Now

$$\frac{du}{dh}\delta h = -\frac{\int\int\int \dots P\chi e^{-h\chi}\, ds\, dx_1 \dots dz_r}{\int\int\int \dots Pe^{-h\chi}\, ds\, dx_1 \dots dz_r}\delta h = -\overline{\chi}\delta h.$$

Also $$\frac{du}{dv}\delta v = \delta \log \int\int \dots (\int Pe^{-h\chi} ds) dx_1 \dots dz_r,$$

where $\delta$ refers to the variation of the limits of integration in the $x$, $y$, and $z$'s.

Now

$$\begin{aligned}
&\delta \log \int\int \dots (\int Pe^{-h\chi} ds) dx_1 \dots dz_r \\
&= \frac{\int\int \dots (\int Pe^{-h\chi} ds)\, \delta dx_1 \dots dz_r}{\int\int \dots (\int Pe^{-h\chi} ds) dx_1 \dots dz_r} \\
&= \frac{\delta \int\int \dots (dx_1 \dots dz_r)}{\int\int \dots (dx_1 \dots dz_r)} \\
&= \frac{\delta v^r}{v^r} = \frac{r\delta v}{v}; \quad *
\end{aligned}$$

$$\therefore \quad \frac{r\delta v}{v} = \overline{\chi}\delta h + \delta u.$$

Also $$\frac{\delta Q}{\tau} = -\frac{r}{h}\delta h + \frac{2h}{3}\delta\overline{\chi} + \tfrac{2}{3} r\delta v.$$

Because $p = \dfrac{r}{vh}$ in this case

$$\therefore \quad \frac{\delta Q}{\tau} = -\frac{r}{h}\delta v + \tfrac{2}{3}\delta(h\overline{\chi}) + \tfrac{2}{3}\delta u$$

$$= \delta\{-r\log h + \tfrac{2}{3} h\overline{\chi} + \tfrac{2}{3}\log \int\int \dots (\int Pe^{-h\chi} ds) dx_1 \dots dz_r\}.$$

When the intermolecular forces are considered, the value of $\dfrac{du}{dv}\delta v$ will consist not only of the term $r\dfrac{\delta v}{v}$ arising from the variation of the limits of integration with regard to the $x$, $y$, and $z$ coordinates, but also of a term arising from the variation

* $\dfrac{du}{dv}\delta v$ is the alteration which would take place in $u$, if the volume were increased in the ratio $\dfrac{v+dv}{v}$, the ratio between the coordinates $x_1 \dots z_r$ remaining unaltered.

of $\chi$ with regard to $v$. This latter term is seen from the value of $u$ to be

$$\frac{-h\int\int\ldots\frac{d\chi}{dv}(\int Pe^{-h\chi}ds)\,dx_1\ldots dz_r}{\int\int\ldots(\int Pe^{-h\chi}ds)\,dx_1\ldots dz_r}\cdot\delta v;$$

$$\text{i.e.}\quad -h\overline{\frac{d\chi}{dv}}\,\delta v;$$

and therefore in this case we have

$$\delta u=-\overline{\chi}\delta h+\frac{r\delta v}{v}-h\overline{\frac{d\chi}{dv}}\,\delta v;$$

$$\therefore\quad \frac{r\delta v}{v}-h\overline{\frac{d\chi}{dv}}\,\delta v=\overline{\chi}\delta h+\delta u.$$

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Also in this case we have

$$pv=\frac{r}{h}-\tfrac{1}{3}\Sigma(\overline{Rr});$$

$$\therefore\quad p\delta v=\frac{r\delta v}{hv}-\frac{\delta v}{3v}\Sigma(\overline{Rr}).$$

But if there be a general cubical expansion in the mass from $v$ to $v+\delta v$, this must correspond to a linear expansion from $r$ to $r+\delta r$, where

$$\frac{\delta r}{r}=\frac{1}{3}\cdot\frac{\delta v}{v};$$

$$\therefore\quad p\delta v=\frac{r\delta v}{vh}-\overline{\Sigma R\delta r}.$$

Now since $R$ is the attractive force between any pair of molecules, $\Sigma(R\delta r)$ for any particular configuration must be the increase of potential energy consequent upon the expansion $\delta v$ in that particular configuration and the mean value of $\Sigma(R\delta r)$ for all possible configurations, or $\overline{\Sigma(R\delta r)}$ must be the mean value of the increases of potential energy for all such configurations, or $\overline{\frac{d\chi}{dv}}\,\delta v$.*

* It is important to distinguish between $\overline{\frac{d\chi}{dv}}$ or the mean value of the rate of increase of potential energy on expansion for all configurations, and $\frac{d\overline{\chi}}{dv}$ or the rate of increase of the mean potential energy; the former is clearly equal to $\frac{1}{3v}\overline{\Sigma(Rr)}$ by what has been said above, and the latter is found by differentiating the expression for $\overline{\chi}$ with regard to $v$.

But $$\frac{\delta Q}{\tau} = -\frac{r}{h}\delta h + \frac{2h}{3}\delta\bar{\chi} + \frac{2h}{3}p\delta v;$$

$$\therefore \quad \frac{\delta Q}{\tau} = -\frac{r}{h}\delta h + \frac{2h}{3}\delta\bar{\chi} + \frac{2}{3}\frac{r\delta v}{v} - \frac{2h}{3}\overline{\frac{d\chi}{dv}}\delta v;$$

$$\therefore \quad \frac{\delta Q}{\tau} = -\frac{r}{h}\delta h + \tfrac{2}{3}(h\overline{\delta\chi} + \bar{\chi}\delta h) + \tfrac{2}{3}\delta u$$

$$= \delta\{-r\log h + \tfrac{2}{3}h\bar{\chi} + \tfrac{2}{3}\log\iint\ldots(\int Pe^{-h\chi}ds)\,dx_1\ldots dz_r\},$$

as before.

It appears therefore that whether there be appreciable intermolecular forces, or not, $\frac{\delta Q}{T}$ will be the exact differential of a function $\phi$ of the independent variables $h$ and $v$, where $\phi$ is equal to

$$-r\log h + \tfrac{2}{3}h\bar{\chi} + \tfrac{2}{3}\log\iint\ldots(\int Pe^{-h\chi}ds)\,dx_1\ldots dz_r.$$

When the molecules become material particles, $P$ must be replaced by unity, and the value of $\phi$ becomes

$$-r\log h + \tfrac{2}{3}h\bar{\chi} + \tfrac{2}{3}\log\iint\ldots e^{-h\chi}dx_1\ldots dz_r,$$

this being the form given by Dr. Boltzmann in the memoir referred to above.*

Again, if we write $d\sigma$ for the product $dx_1\ldots dz_r$, we get

$$\bar{\chi} = \frac{\iint\ldots\chi Pe^{-h\chi}ds\,d\sigma}{\iint\ldots Pe^{-h\chi}ds\,d\sigma};$$

$$\therefore \quad \frac{d\bar{\chi}}{dv} = \frac{\iint\ldots\frac{d\chi}{dv}Pe^{-h\chi}ds\,d\sigma}{\iint\ldots Pe^{-h\chi}ds\,d\sigma} + \frac{\iint\ldots(-h\chi)\frac{d\chi}{dv}Pe^{-h\chi}ds\,d\sigma}{\iint\ldots Pe^{-h\chi}ds\,d\sigma}$$

$$+ \frac{\iint\ldots\chi Pe^{-h\chi}ds\,d\sigma\iint\ldots(-hP\frac{d\chi}{dv})e^{-h\chi}ds\,d\sigma}{(\iint\ldots Pe^{-h\chi}ds\,d\sigma)^2}.$$

But $$\overline{\frac{d\chi}{dv}} = \frac{\iint\ldots\frac{d\chi}{dv}Pe^{-h\chi}ds\,d\sigma}{\iint\ldots Pe^{-h\chi}ds\,d\sigma}.$$

$$\therefore \quad \frac{d}{dh}\left(\overline{\frac{d\chi}{dv}}\right) = \frac{\iint\ldots(-\chi)\frac{d\chi}{dv}Pe^{-h\chi}ds\,d\sigma}{\iint\ldots Pe^{-h\chi}ds\,d\sigma}$$

$$+ \frac{\iint\ldots\chi Pe^{-h\chi}ds\,d\sigma\iint\ldots(-P)\frac{d\chi}{dv}e^{-h\chi}ds\,d\sigma}{(\iint\ldots Pe^{-h\chi}ds\,d\sigma)^2};$$

* The proof given above of the second law of thermodynamics on the principles of the kinetic theory of gases is due to Mr. S. H. Burbury, M.A., formerly Fellow of St. John's College, Cambridge, and was published in the Philosophical Magazine for January, 1876.

$$\therefore \quad \frac{d\overline{\chi}}{dv} = \overline{\frac{d\chi}{dv}} + h\frac{d}{dh}\left(\overline{\frac{d\chi}{dv}}\right) = \left(h\frac{d}{dh} + 1\right)\overline{\frac{d\chi}{dv}}.$$

Now if $\tau$ be the temperature, we have

$$\tau = \frac{3}{2h};$$

$$\therefore \quad \left(\tau\frac{d}{d\tau} - 1\right) = -\left(h\frac{d}{dh} + 1\right).$$

But $$p = \frac{r}{vh} - \overline{\frac{d\chi}{dv}}$$ (see note p. 49)

$$\therefore \quad -\left(h\frac{d}{dh} + 1\right)p = -\left(h\frac{d}{dh} + 1\right)\overline{\frac{d\chi}{dv}} = -\frac{d\overline{\chi}}{dv}.$$

But $$h\frac{d}{dh} + 1 = -\left(\tau\frac{d}{d\tau} - 1\right);$$

$$\therefore \quad \frac{d\overline{\chi}}{dv} = \tau\frac{dp}{d\tau} - p;$$

$$\therefore \quad \delta\overline{\chi} = \delta\int\left(\tau\frac{dp}{d\tau} - p\right)dv.$$

Now $$\delta Q = r\delta\tau + \delta\overline{\chi} + p\delta v;$$

therefore $$\delta Q = r\delta\tau + \delta\int\left(\tau\frac{dp}{d\tau} - p\right)dv + pdv.$$

The expression obtained by Rankine and other writers upon thermodynamics.

*May*, 1877.

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