For those simple gases which manifest no irregularities with respect to their volume, and for those compound ones which suffered no diminution of volume during the act of combination, γ, and therefore K/H also, has the same value. For these gases we have approximately

$$\frac{\gamma'}{\gamma} = 1\cdot421,$$

hence

$$\frac{K}{H} = 0\cdot6315.$$

On the contrary, for those compound gases whose volumes during combination have been diminished, γ is greater, and consequently K/H less; and, in fact, it is less the smaller the volume of the combination compared with the sum of the volumes of its constituents, the latter being all considered gaseous.

Thus it is corroborated what was before stated, that the *vis viva* of the translatory motion does not alone represent the whole quantity of heat in the gas, and that the difference is greater the greater the number of atoms of which the several molecules of the combination consist. We must conclude, therefore, that besides the translatory motion of the molecules as such, the constituents of these molecules perform other motions, whose *vis viva* also forms a part of the contained quantity of heat.

Zurich, January 5, 1857.

9

On the Mean Lengths of the Paths Described by the Separate Molecules o' Gaseous Bodies*

RUDOLF CLAUSIUS

SUMMARY

The theory of gases proposed by Joule, Krönig and Clausius preceding selection) was criticized on the ground that if the molecules r move great distances in straight lines, then two gases in contact with other would rapidly mix, in contrast to experience. The objection ma answered by taking account of the fact that real gases are not " id and therefore the portion of the time during which molecular forces ; not vanishingly small compared with the entire path of a molecule quantitative theory may be constructed if one assumes the molecul be characterized by a certain distance ρ, such that if the centres of gr of two molecules pass by each other at a distance greater than ρ intermolecular repulsive forces do not come into play and there is o slight deflection resulting from attractive forces, while if the distan less than ρ the repulsive forces cause the molecules to rebound from other. The spherical volume of radius ρ around the molecule is calle *sphere of action* of the molecule. We ask: how far on an average c

molecule move before its centre of gravity comes into the sphere of action of another molecule? This average distance is called the mean free path l.

It is shown that the mean length of path of a molecule is in the same proportion to the radius of the sphere of action as the entire space occupied by the gas, to that portion of the space which is actually filled up by the spheres of action of the molecules: $l/\rho = V/(\frac{4}{3}\pi\rho^3)$. (It is assumed that all the molecules move with the same velocity.) For example, if this ratio is taken to be 1000:1, and the average distance between molecules is $\lambda = V^{1/3}$, we find that $l = 62\lambda$. Although the number of molecules in a given volume of gas is as yet unknown, we must assume that it is quite large, and that λ is very small compared to our usual units of length. Thus it is plausible that the mean path is really quite small, and the objection cited is not valid.

(1.) The February number of Poggendorff's *Annalen* contains a paper by Buijs-Ballot " On the Nature of the Motion which we call Heat and Electricity."† Amongst the objections which the author there makes against the views advanced by Joule, Krönig and myself concerning the molecular motion of gaseous bodies, the following deserves especial consideration. Attention is drawn to the circumstance that, if the molecules moved in straight lines, volumes of gases in contact would necessarily speedily mix with one another,—a result which does not actually take place. To prove that such mixture does not occur, the following facts are adduced (p. 250):— " How then does it happen that tobacco-smoke, in rooms, remains so long extended in immoveable layers?" Mention is also made of the same appearance with clouds of smoke in the open air. Further, " If sulphuretted hydrogen or chlorine be evolved in one corner of a room, entire minutes elapse before they are smelt in another corner, although the particles of gas must have had to traverse the room hundreds of times in a second." Further, " How could carbonic acid gas remain so long in an open vessel?"

These objections may, at first glance, appear to have very great weight; and I consider it therefore necessary to prove, by special considerations, that the facts adduced are perfectly reconcileable with the theory of the rectilineal motion of the molecules. Indeed, I rejoice at the discussion of this point by M. Buijs-Ballot, inasmuch

† C. H. D. Buijs-Ballot (Buys-Ballot), *Ann. Phys.* **103**, 240 (1858).

as it affords me a desired opportunity of completing this part of m theory (which was perhaps discussed too briefly in my paper), and 1 prevent thereby further misunderstandings.

(2.) It is assumed in the objections, that the molecules traver: considerable spaces in straight lines; this appears prominently in th second objection, in which it is said that a molecule must have had 1 traverse the room many times in a second. This assumption ca: however, in nowise be considered as a necessary consequence of th views advanced by me concerning the conditions of gases. Among the conditions which must be satisfied if Mariotte and Gay-Lussac law for a gas is true with perfect strictness, I have adduced the fc lowing,—" that those portions of the path of a molecule througho: which the molecular forces are of influence in sensibly altering th motion of the molecule, either in direction or velocity, must be vanishing value compared with those portions of the path throug out which such forces may be considered as inactive." Now actually existing gases, Mariotte and Gay-Lussac's law is not strictl but only approximately true; and it hence follows that in them suc first portions of the paths of the molecules must be small, but n vanishingly small, compared with the entire paths. Inasmuch, nov as one of the fundamental conditions upon which the whole theo1 rests is that the molecular forces are only effective at small distanc from the molecules, a path which is very great in comparison to th sphere of action of a molecule may yet, considered absolutely, 1 very small.

By a few simple considerations, an approximate idea may 1 formed of the mean magnitude of the paths traversed by the separa molecules: I purpose endeavouring to elucidate this in wh immediately follows.

(3.) For this purpose it will be advisable to prefix some remar1 concerning the manner in which it is possible to view the molecul: forces, and what has accordingly to be understood by the sphere action. These remarks are not to be considered as an essential pa of the subsequent development, but are merely intended to fix o1 ideas.

If we do not take into account the forces of chemical affinity, a1 only consider such molecules as are chemically indifferent to o1 another, I imagine that there are still two forces which are to 1

distinguished. I believe, namely, that when two molecules approach one another an attraction is at first exerted, which begins to be of sensible effect even at some distance, and which increases as the distance diminishes; but that, when the molecules have arrived into the immediate neighbourhood of one another, a force comes into play which seeks to drive them asunder. For the view which it is here intended to take, it is indifferent what kind of force this repulsive one is supposed to be, that is, whether, as in the case of solid elastic bodies, it only strives to separate the molecules when they are in actual contact with a force equal to that with which they are pressed together, or whether it is one which begins to act before the actual contact of the molecules. In the same manner, we need not here discuss the question as to the source of these forces, whether they are both to be ascribed to the particles of ponderable matter themselves, or whether one of them is to be referred to a more subtle substance, with which the ponderable particles of matter are furnished.

Let us now imagine two molecules moving in directions such that, if they preserved them unchanged, they would not strike one another, but pass by at some distance. Two cases may here occur. If the distance is very small, the molecules which were drawn towards one another, even from some distance, by the force of attraction, approach so closely that the repulsive force comes into play, and a rebounding of the molecules results. If the distance be somewhat greater, the paths of the molecules only suffer a certain change of direction through the attractive force, without the repulsive force being able to act. Finally, at still greater distances, the effect of the molecules upon one another may be altogether neglected.

How great the distances must be in order that the one or other case might occur, could not be determined universally, even if we possessed exact knowledge of the molecular forces; for the velocity of the molecules and the reciprocal inclination of their paths are of influence. Nevertheless, *mean* values of these distances may be obtained. We will therefore suppose that the distance ρ is given for such a mean value, which forms the boundary between the first and second case, and the meaning of which we will define with greater precision in the following manner:—If the centres of gravity of two molecules have such directions of motion that if they were to proceed

in those directions in straight lines they would pass by one another a distance greater than ρ, then the molecules only change t courses to some extent through reciprocal attraction, without repulsive force coming into action between them. If, on the o hand, this distance is less than ρ, the latter force also comes into p and a rebounding of the molecules takes place.

If, now, the latter case alone be considered as one of *impact*, we do not concern ourselves with the changes of direction which force of attraction effects at greater distances, we may, for what have here to consider, represent a sphere of radius ρ, descri around a molecule and having its centre of gravity for a centre the term *sphere of action* of the molecule.

I again call attention to the fact that the special hypotheses l made, concerning the nature of the molecular forces, are not to viewed as a necessary condition for the developments which foll their only purpose is to facilitate the comprehension by giving so thing definite to the imagination. It is of no import how we consi the forces by reason of which the molecules change the direction their motions; if we but admit that their effects are only sensibl very small distances, we may assume some distances as limiting va for the purpose of being able to neglect the actions from gre distances, and only regard those for smaller ones. A sphere descri at this distance may be called a sphere of action.

(4.) If, now, in a given space, we imagine a great number molecules moving irregularly about amongst one another, and if select one of them to watch, such a one would ever and anon impi upon one of the other molecules, and bound off from it. We h now, therefore, to solve the question as to how great is the m length of the path between two such impacts; or more exa expressed, *how far on an average can the molecule move, before centre of gravity comes into the sphere of action of another molec*

We will not discuss this question, however, immediately in form just given: we will propose instead a somewhat simpler o which is related to the other in such a manner that the solution of one may be derived from that of the other.

If we assume that not all the molecules present in the space are motion, but that the one chosen for observation is the only which moves, and all the rest remain fixed in position, the mov

molecule in these circumstances also would strike here and there upon one of the others, and the number of blows which it suffers in this case during one unit of time may be compared with the numbers which it would experience in event of universal movement. On considering the matter more attentively, we are soon convinced that the number of blows amongst moving molecules must be greater than amongst stationary ones, or, which comes to the same thing, that the mean length of the paths which the molecule watched passes over between two consecutive impacts, must be less in the first case than in the second. The relation between the lengths of the two paths may be definitely found as soon as the velocity of the remaining molecules, in comparison with that of the one watched, is known. For our investigations, that case only is of special interest where the velocities of all the molecules are *on an average* equally great. In this case, if we only consider the *mean* velocities, we may more simply assume that all molecules move at the same rate; and for this case we obtain the following result:—*The mean lengths of path for the two cases* (1) *where the remaining molecules move with the same velocity as the one watched*; and (2) *where they are at rest, bear the proportion to one another of* $\frac{3}{4}$ *to* 1.

It would not be difficult to prove the correctness of this relation: it is, however, unnecessary for us to devote our time to it; for, in our consideration of the mean path, it is not the question to determine exactly its numerical value, but merely to obtain an approximate notion of its magnitude; and hence the exact knowledge of this relation is not necessary. It is even sufficient for our purpose if we may assume as certain that the mean path among moving molecules *cannot be greater* than among stationary ones; this will certainly be at once admitted. Under this hypothesis, we will confine the discussion of the question to that case *where the molecule watched alone moves, while all the others remain at rest.*

Moreover, without affecting the question in anything, we may suppose a mere moving point in place of the moving molecule; for it is in fact only the centre of gravity of the molecule which has to be considered.

(5.) Suppose, then, there is a space containing a great number of molecules, and that these are not regularly arranged, the only condition being that the density is the same throughout, *i.e.* in equal

parts of the space there are the same numbers of molecules. determination of the density may be performed conveniently fo investigation by knowing how far apart two neighbouring mole would be separated from one another if the molecules were arra cubically, that is, so arranged that the whole space might be posed divided into a number of equal very small cubic space whose corners the centres of the molecules were situated. We denote this distance, that is, the side of one of these little cube λ, and shall call it *the mean distance of the neighbouring molecu.*

If, now, a point moves through this space in a straight line, l suppose the space to be divided into parallel layers perpendicul the motion of the point, and let us determine *how great is the bability that the point will pass freely through a layer of the thickr. without encountering the sphere of action of a molecule.*

Let us first take a layer of the thickness 1, and let us denote b fraction of unity a the probability of the point passing throug layer without meeting with any sphere of action: then the c sponding probability for a thickness 2 is a^2; for if such a lay supposed divided into two layers of the thickness 1, the probal of the points passing free through the first layer, and thereby arr at the second, must be multiplied by the probability of its pa through the latter one. Similarly, for a layer of the thickness ? have a^3, &c., and for a layer of any thickness x we may accord write a^x. Let us transform this expression by putting e^{-a} for which e is the base of the natural logarithms, and $-\alpha = l$ which logarithm must be negative, because a is less than 1. If we denote the probability of the free passage through a layer o thickness x by W, we have the equation

$$W = e^{-\alpha x},$$

and we have only to determine here the constant α.

Again, let us consider a layer of such thinness that the hi powers of the thickness may be neglected in comparison wit first. Calling this thickness δ and the corresponding probability the former equation becomes

$$W_\delta = e^{-\alpha\delta} = 1 - \alpha\delta .$$

The probability in this case may also be determined from special considerations. Let us direct our attention to any plane in the layer parallel to one of the bounding planes of the layer, and let us suppose all the molecules whose centres lie in the layer to be so moved perpendicular to the layer that their centres all fall upon this plane; we have now only to inquire how great the probability is that the point, in its passage through this plane, meets with no sphere of action; such probability may be simply represented by the proportion of two superficial areas. Of the entire part of the plane which falls within the given space, a certain portion is covered by the great circles of the spheres of action whose centres fall upon it, while the remaining portion is free for the passage; and the probability of the uninterrupted passage is therefore expressed *by the relation of the free portion of the plane to the whole plane.*

From the manner in which the density was determined at the beginning of this article, it follows that in a layer of thickness λ, so many molecules must be contained, that, if they be supposed brought into one and the same plane parallel to the bounding plane, and to be arranged still quadratically in this plane, then the side of the small square in whose corners would be situated the centres of the molecules would be equal to λ. Hence it follows, that the part of the plane which would be covered by the great circles of the spheres of action, would be related to the remainder of the plane as a great circle would to a square of side λ, so that, accordingly, the covered superficial area would be expressed by the fraction

$$\frac{\pi\rho^2}{\lambda^2}$$

of the entire superficial area. In order to ascertain the corresponding magnitude for a layer of the thickness δ, we have only to multiply the previous fraction by δ/λ, that is,

$$\frac{\pi\rho^2}{\lambda^3}\delta;$$

and if this magnitude be subtracted from 1, the difference represents the free portion of the plane as a fraction of the whole plane.

Hence the probability that the point will pass through our] or, which comes to the same thing, through a layer of thickn without obstruction, is determined by the equation

$$W_\delta = 1 - \frac{\pi\rho^2}{\lambda^3}\delta;$$

and on comparing this expression for W_δ with that given in equ (2), we find that

$$\alpha = \frac{\pi\rho^2}{\lambda^3},$$

and hence the general equation (1) is transformed into

$$W = e^{-(\pi\rho^2/\lambda^3)\,x}.$$

(6.) By means of this equation we can now determine the value of the path which the point has to traverse before it meet a sphere of action.

Let us suppose that a great number (N) of points are th through space in one direction, and let us suppose the space divided into very thin layers perpendicular to the directic motion; then a small number of the points would be detained first layer by the spheres of action, another lot in the second, an in the third, and so on. If, now, each of these small numbe multiplied by the length of path, the products added, and the obtained divided by the whole number N, the quotient will t mean length of the path which we seek.

According to equation (5), the number of points which reach or pass the distance x from the commencement of the m is represented by

$$Ne^{-(\pi\rho^2/\lambda^3)x};$$

and accordingly the number which reach or pass the dis $x + dx$ is expressed by

$$Ne^{-(\pi\rho^2/\lambda^3)(x + dx)} = Ne^{-(\pi\rho^2/\lambda^3)\,x}\left(1 - \frac{\pi\rho^2}{\lambda^3}dx\right).$$

The difference of these two expressions, namely,

$$Ne^{-(\pi\rho^2/\lambda^3)\,x} \cdot \frac{\pi\rho^2}{\lambda^3}dx,$$

represents the number of those points which are detained between x and $x + dx$. The path traversed by these points may be considered as x if we neglect infinitely small differences; and hence the above expression must be multiplied by this length in order to obtain one of the products mentioned before, namely,

$$Ne^{-(\pi\rho^2/\lambda^3)x} \cdot \frac{\pi\rho^2}{\lambda^3} \, xdx.$$

If, now, it be desired to obtain the sum of all products of this kind which correspond to the several layers of the thickness dx, this must of course, in the case in point where the layers are infinitely thin, be effected by integration. Hence the above formula has to be integrated from $x = 0$ to $x = \infty$, whence the following expression is obtained,

$$N\frac{\lambda^3}{\pi\rho^2}.$$

This expression has now only to be divided by N in order to arrive at the mean length of path required. If this be called l', the equation is

$$l' = \frac{\lambda^3}{\pi\rho^2}. \tag{6}$$

In the case where not one molecule only is in motion while all the others are at rest, but where all molecules move with equal velocity, the mean length of way, as mentioned before, is less than that above considered in the proportion of $\frac{3}{4}$ to 1. Hence if we put the simple letter l for this case, we have

$$l = \frac{3}{4}\frac{\lambda^3}{\pi\rho^2}. \tag{7}$$

Writing this equation in the form

$$\frac{l}{\rho} = \frac{\lambda^3}{\frac{4}{3}\pi\rho^3}, \tag{7a}$$

a simple law results. It follows from the manner in which we determined the density, that the part of the given space filled by the spheres of action of the molecules is related to the whole given space as a sphere of action to a cube of the side λ, that is, as

$$\tfrac{4}{3}\pi\rho^3 : \lambda^3.$$

Accordingly the meaning of the previous equation may be so put: *The mean length of path of a molecule is in the same proportion to t radius of the sphere of action as the entire space occupied by the g to that portion of the space which is actually filled up by the spheres action of the molecules.*

(7.) In order to have a definite numerical example, let us assum in round numbers, that the spheres of action of the molecules are small that only a thousandth of the space occupied by the gas really filled out by the spheres of action, and that the whole remaini space be free for motion.

For this case we have

$$\frac{\lambda^3}{\frac{4}{3}\pi\rho^3} = 1000,$$

whence it follows that

$$\frac{\lambda}{\rho} = 16\cdot12.$$

On applying these values we obtain from equations (6) and (7),

$$l' = 1333\rho = 83\lambda,$$

$$l = 1000\rho = 62\lambda.$$

The first expressions in both equations show that, under the a sumption made, the mean path has a considerable length in co parison to the radius of the spheres of action, and that therefore, far as the effect of this circumstance is concerned, Mariotte and G Lussac's law may be very nearly true for the gas. By a simple calcu tion it may be shown that the relation of 1000 to 1 completely suffic even for those approximations found by Regnault with permane gases. It follows that the magnitude of the spheres of action whi was taken for illustration, although arbitrarily chosen, may yet regarded as one within the bounds of possibility.

But if we now regard this same mean value of the length of path such a manner as to compare it, not with the sizes of molecules, t with our usual units of length, we obtain totally different relatio In all physical and chemical investigations in which opportun presents itself for drawing conclusions concerning the weight a size of the separate molecules, we are invariably led to the conclusi

that, compared with all measurable magnitudes, molecules must be of extraordinarily small size. As yet, no one has been able to establish a bounding line on the other side (for smallness). Accordingly, when an ordinary unit of measure, *e.g.* a litre, is filled with gas at the ordinary atmospheric pressure, we must assume that the number of molecules present is very great, and that consequently the distances between the molecules is very small. Accordingly the values previously found for l' and l, namely, 83λ and 62λ, must only be regarded as small magnitudes.

(8.) After the above determination of the length of the *mean* path, we still have to consider how the separate paths which really occur are related to the mean path.

The first question which presents itself is, in what proportion is the number of cases in which the real path is less than the mean path, to that of the cases in which it is greater. For answering this question, use is made of (5), in which we have only to substitute the mean value l' for x in order to find what probability there is that the true path is equal to or greater than the mean one. If for l' we here make use of the expression in (6), and denote the corresponding value of W by W_1, then

$$W_1 = e^{-1} = 0.3679. \qquad (11)$$

From the above equation it follows, that out of N cases only $0.3679\ N$ occur in which the real path is equal to, or greater than the mean one, while in the

$$0.6321\ N$$

cases the true path is the smaller one.

If, further, it be required to know the number of cases in which the true path is equal to or above the double, treble, &c. of the mean one, the same process may be adopted as before. Calling the probabilities in question W_2, W_3, &c., we have

$$\left.\begin{array}{l} W_2 = e^{-2} \\ W_3 = e^{-3} \\ \&c. \end{array}\right\} \qquad (12)$$

These numbers evidently diminish very rapidly, since, for instance, $e^{-10} = 0.000045$; and we gather from this that, although in isolated

cases a molecule may traverse a path considerably longer tha[n] mean one, such cases are comparatively rare, and that in the ma[ss] of cases the actual path is smaller or very little larger than the mean value found above.

(9.) If, now, these results be applied to the externally recogni[sed] behaviours of a gas, in which it is presumed that no other m[otion] common to the whole mass besides the molecular one is presen[t,] easy to convince oneself that the theory which explains the expa[nsive] force of gases does not lead to the conclusion that two quantit[ies of] gas bounding one another must mix with one another quickl[y and] violently, but that only a comparatively small number of atom[s] arrive quickly at a great distance, while the chief quantities gradually mix at the surface of their contact.

From this it is clear why clouds of smoke only slowly lose form on quiet days. Even when the air is in motion, provided motion consists of a uniform one of the entire current, a clo[ud of] smoke may be carried off without quickly losing its form. B[ut] other facts adduced by Buijs-Ballot also admit of simple explan[ation.] The remark made by him attached to one of his objections, th[at] molecules of gas in a room must traverse the room many hu[ndred] times in one second, is completely foreign to the theory. Perh[aps it] might be said of a remark which occurs in the mathematical dev[elop-] ment attached to my previous paper, that it afforded reason for an idea. I assumed there, namely, that the gas was in a ver[y] vessel, and I then assumed that the molecules of gas without di[sturb-] ing one another, sped backwards and forwards between the two parallel sides. Nevertheless, this assumption was there intro[duced] with the following words: " In estimating the pressure, *inste[ad of] regarding the motion as it really occurs*, we may introduce c[ertain] simplifications." I believe I thereby called sufficient attention [to the] fact that this assumption should not serve to furnish an image [of the] real process, but only to simplify the calculation there intende[d, the] result of which could not be thereby changed.

10

Illustrations of the Dynamical Theory of Gases *

JAMES CLERK MAXWELL

SUMMARY

In view of the current interest in the theory of gases proposed by Bernoulli (Selection 3), Joule, Krönig, Clausius (Selections 8 and 9) and others, a mathematical investigation of the laws of motion of a large number of small, hard, and perfectly elastic spheres acting on one another only during impact seems desirable.

It is shown that the number of spheres whose velocity lies between v and $v + dv$ is

$$N \frac{4}{\alpha^3 \sqrt{\pi}} v^2 e^{-v^2/\alpha^2} dv,$$

where N is the total number of spheres, and α is a constant related to the average velocity:

$$\text{mean value of } v^2 = \tfrac{3}{2} \alpha^2.$$

If two systems of particles move in the same vessel, it is proved that the mean kinetic energy of each particle will be the same in the two systems.

Known results pertaining to the mean free path and pressure on the surface of the container are rederived, taking account of the fact that the velocities are distributed according to the above law.

The internal friction (viscosity) of a system of particles is predicted to be independent of density, and proportional to the square root of the

absolute temperature; there is apparently no experimental evide confirm this prediction for real gases.

A discussion of collisions between perfectly elastic bodies of an leads to the conclusion that the final equilibrium state of any num systems of moving particles of any form is that in which the a kinetic energy of translation along each of the three axes is the sam the systems, and equal to the average kinetic energy of rotation abot of the three principal axes of each particle (equipartition theorem) mathematical result appears to be in conflict with known experi values for the specific heats of gases.

PART I

On the Motions and Collisions of Perfectly Elastic Sphere.

So many of the properties of matter, especially when in the g form, can be deduced from the hypothesis that their minute pa in rapid motion, the velocity increasing with the temperature the precise nature of this motion becomes a subject of ra curiosity. Daniel Bernoulli, Herapath, Joule, Krönig, Cla etc.† have shewn that the relations between pressure, tempe and density in a perfect gas can be explained by supposir particles to move with uniform velocity in straight lines, st against the sides of the containing vessel and thus producing sure. It is not necessary to suppose each particle to travel great distance in the same straight line; for the effect in pro pressure will be the same if the particles strike against each so that the straight line described may be very short. M. Cla has determined the mean length of path in terms of the avera; tance of the particles, and the distance between the centres particles when collision takes place. We have at present no me ascertaining either of these distances; but certain phenomena as the internal friction of gases, the conduction of heat through and the diffusion of one gas through another, seem to indic possibility of determining accurately the mean length of path a particle describes between two successive collisions. In or

† See the Bibliography and Selections 3, 8 and 9 in this volume.

‡ See Selection 9.