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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

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

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

PART I

On the Motions and Collisions of Perfectly Elastic Spheres.

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

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

‡ See Selection 9.

lay the foundation of such investigations on strict mechanical principles, I shall demonstrate the laws of motion of an indefinite number of small, hard, and perfectly elastic spheres acting on one another only during impact.

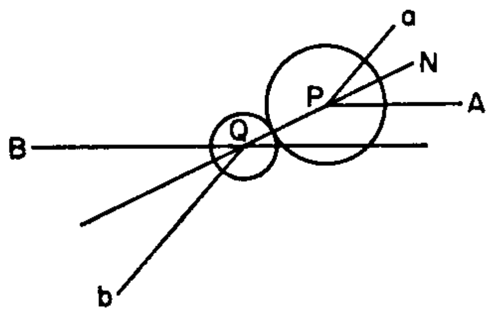
If the properties of such a system of bodies are found to correspond to those of gases, an important physical analogy will be established, which may lead to more accurate knowledge of the properties of matter. If experiments on gases are inconsistent with the hypothesis of these propositions, then our theory, though consistent with itself, is proved to be incapable of explaining the phenomena of gases. In either case it is necessary to follow out the consequences of the hypothesis.

Instead of saying that the particles are hard, spherical, and elastic, we may if we please say that the particles are centres of force, of which the action is insensible except at a certain small distance, when it suddenly appears as a repulsive force of very great intensity. It is evident that either assumption will lead to the same results. For the sake of avoiding the repetition of a long phrase about these repulsive forces, I shall proceed upon the assumption of perfectly elastic spherical bodies. If we suppose those aggregate molecules which move together to have a bounding surface which is not spherical, then the rotatory motion of the system will store up a certain proportion of the whole *vis viva*, as has been shewn by Clausius, and in this way we may account for the value of the specific heat being greater than on the more simple hypothesis.

On the Motion and Collision of Perfectly Elastic Spheres.

Prop. I. Two spheres moving in opposite directions with velocities inversely as their masses strike one another; to determine their motions after impact.

Let P and Q be the position of the centres at impact; AP, BQ the directions and magnitudes of the velocities before impact; Pa, Qb the same after impact; then, resolving the velocities parallel and perpendicular to PQ the line of centres, we find that the velocities parallel to the line of centres are exactly reversed, while those perpendicular to that line are unchanged. Compounding these velocities again, we find that the velocity of each ball is the same before and after impact, and that the directions before and after impact lie in the same plane with the line of centres, and make equal angles with it.



Prop. II. To find the probability of the direction of the velocity after impact lying between given limits.

In order that a collision may take place, the line of motion of one of the balls must pass the centre of the other at a distance less than the sum of their radii; that is, it must pass through a circle whose centre is that of the other ball, and radius (s) the sum of the radii of the balls. Within this circle every position is equally probable, and therefore the probability of the distance from the centre being between r and $r + dr$ is

$$\frac{2rdr}{s^2}.$$

Now let ϕ be the angle APa between the original direction and the direction after impact, than $APN = \frac{1}{2}\phi$, and $r = s \sin \frac{1}{2}\phi$, and the probability becomes

$$\tfrac{1}{2} \sin \phi d\phi.$$

The area of a spherical zone between the angles of polar distance ϕ and $\phi + d\phi$ is

$$2\pi \sin \phi d\phi;$$

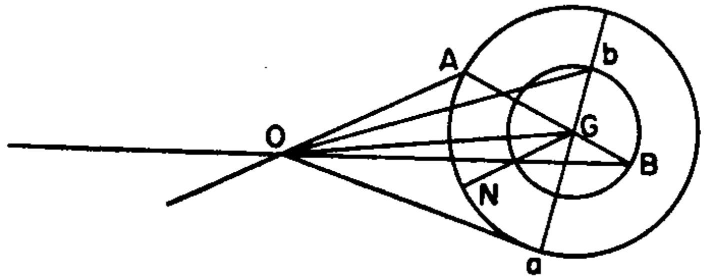
therefore if ω be any small area on the surface of a sphere, radius unity, the probability of the direction of rebound passing through this area is

$$\frac{\omega}{4\pi};$$

so that the probability is independent of ϕ, that is, all directions of rebound are equally likely.

Prop. III. Given the direction and magnitude of the velocities of two spheres before impact, and the line of centres at impact; to find the velocities after impact.

Let OA, OB represent the velocities before impact, so that if there had been no action between the bodies they would have been at A and B at the end of a second. Join AB, and let G be their centre of



gravity, the position of which is not affected by their mutual action. Draw GN parallel to the line of centres at impact (not necessarily in the plane AOB). Draw aGb in the plane AGN, making $NGa = NGA$, and $Ga = GA$ and $Gb = GB$; then by Prop. I. Ga and Gb will be the velocities relative to G; and compounding these with OG, we have Oa and Ob for the true velocities after impact.

By Prop. II. all directions of the line aGb are equally probable. It appears therefore that the velocity after impact is compounded of the velocity of the centre of gravity, and of a velocity equal to the velocity of the sphere relative to the centre of gravity, which may with equal probability be in any direction whatever.

If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision; so that after a certain time the *vis viva* will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable, though the velocity of each particle changes at every collision.

Prop. IV. To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles.

Let N be the whole number of particles. Let x, y, z be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which x lies between x and $x + dx$, be $Nf(x)dx$, where $f(x)$ is a function of x to be determined.

The number of particles for which y lies between y and $y + dy$ will be $Nf(y)dy$; and the number for which z lies between z and $z + dz$ will be $Nf(z)dz$, where f always stands for the same function.

Now the existence of the velocity x does not in any way affect that of the velocities y or z, since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and $x + dx$, and also between y and $y + dy$, and also between z and $z + dz$, is

$$Nf(x)f(y)f(z)dx\,dy\,dz.$$

If we suppose the N particles to start from the origin at the same instant, then this will be the number in the element of volume $(dx\,dy\,dz)$ after unit of time, and the number referred to unit of volume will be

$$Nf(x)f(y)f(z).$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2).$$

Solving this functional equation, we find

$$f(x) = Ce^{Ax^2}, \quad \phi(r^2) = C^3e^{Ar^2}.$$

If we make A positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make A negative and equal to $-1/\alpha^2$, so that the number between x and $x + dx$ is

$$NCe^{-(x^2/\alpha^2)}\,dx.$$

Integrating from $x = -\infty$ to $x = +\infty$, we find the whole number of particles,

$$NC\sqrt{\pi}\alpha = N, \quad \therefore C = \frac{1}{\alpha\sqrt{\pi}},$$

$f(x)$ is therefore $$\frac{1}{\alpha\sqrt{\pi}}\,e^{-(x^2/\alpha^2)}\,.$$

Whence we may draw the following conclusions:—

1st. The number of particles whose velocity, resolved in a certain direction, lies between x and $x + dx$ is

$$N\frac{1}{\alpha\sqrt{\pi}}\,e^{-(x^2/\alpha^2)}\,dx. \tag{1}$$

2nd. The number whose actual velocity lies between v and $v + dv$ is

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

3rd. To find the mean value of v, add the velocities of all the particles together and divide by the number of particles; the result is

$$\text{mean velocity} = \frac{2\alpha}{\sqrt{\pi}}\,. \tag{3}$$

4th. To find the mean value of v^2, add all the values together and divide by N,

$$\text{mean value of } v^2 = \tfrac{3}{2}\alpha^2. \tag{4}$$

This is greater than the square of the mean velocity, as it ought to be.

It appears from this proposition that the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the "method of least squares." The velocities range from 0 to ∞, but the number of those having great velocities is comparatively small. In addition to these velocities, which are in all directions equally, there may be a general motion of translation of the entire system of particles which must be compounded with the motion of the particles relatively to one another. We may call the one the motion of translation, and the other the motion of agitation.

Prop. V. Two systems of particles move each according to the law stated in Prop. IV.; to find the number of pairs of particles, one of each system, whose relative velocity lies between given limits.