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I. *Nineteenth Century Clouds over the Dynamical Theory of Heat and Light* *. *By* The Right. Hon. Lord KELVIN, *G.C.V.O., D.C.L., LL.D., F.R.S., M.R.I.* †.

[IN the present article, the substance of the lecture is reproduced—with large additions, in which work commenced at the beginning of last year and continued after the lecture, during thirteen months up to the present time, is described—with results confirming the conclusions and largely extending the illustrations which were given in the lecture. I desire to take this opportunity of expressing my obligations to Mr. William Anderson, my secretary and assistant, for the mathematical tact and skill, the accuracy of geometrical drawing, and the unfailingly faithful perseverance in the long-continued and varied series of drawings and algebraic and arithmetical calculations, explained in the following pages. The whole of this work, involving the determination of results due to more than five thousand individual impacts, has been performed by Mr. Anderson.—K., Feb. 2, 1901.]

§ 1. THE beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds. I. The first came into existence with the undulatory theory of light, and

* Lecture delivered at the Royal Institution of Great Britain, on Friday, April 27, 1900.

† Communicated by the Author.

was dealt with by Fresnel and Dr. Thomas Young; it involved the question, How could the earth move through an elastic solid, such as essentially is the luminiferous ether? II. The second is the Maxwell-Boltzmann doctrine regarding the partition of energy.

§ 2.—CLOUD I.—RELATIVE MOTION OF ETHER AND PONDERABLE BODIES; such as movable bodies at the earth's surface, stones, metals, liquids, gases; the atmosphere surrounding the earth; the earth itself as a whole; meteorites, the moon, the sun, and other celestial bodies. We might imagine the question satisfactorily answered, by supposing ether to have practically perfect elasticity for the exceedingly rapid vibrations, with exceedingly small extent of distortion, which constitute light; while it behaves almost like a fluid of very small viscosity, and yields with exceedingly small resistance, practically no resistance, to bodies moving through it as slowly as even the most rapid of the heavenly bodies. There are, however, many very serious objections to this supposition; among them one which has been most noticed, though perhaps not really the most serious, that it seems incompatible with the known phenomena of the aberration of light. Referring to it, Fresnel, in his celebrated letter* to Arago, wrote as follows:

"Mais il paraît impossible d'expliquer l'aberration des "étoiles dans cette hypothèse; je n'ai pu jusqu'à présent "du moins concevoir nettement ce phénomène qu'en sup- "posant que l'éther passe librement au travers du globe, "et que la vitesse communiquée à ce fluide subtil n'est "qu'une petite partie de celle de la terre; n'en excède pas "le centième, par exemple.

"Quelque extraordinaire que paraisse cette hypothèse au "premier abord, elle n'est point en contradiction, ce me "semble, avec l'idée que les plus grands physiciens se sont "faite de l'extrême porosité des corps."

The same hypothesis was given by Thomas Young, in *his* celebrated statement that ether passes through among the molecules or atoms of material bodies like wind blowing through a grove of trees. It is clear that neither Fresnel nor Young had the idea that the ether of their undulatory theory of light, with its transverse vibrations, is essentially an elastic solid, that is to say, matter which resists change of shape with permanent or sub-permanent force. If they had

* *Annales de Chimie*, 1818; quoted in full by Larmor in his recent book, 'Æther and Matter,' pp. 320-322.

grasped this idea, they must have noticed the enormous difficulty presented by the laceration which the ether must experience if it moves through pores or interstices among the atoms of matter.

§ 3. It has occurred to me that, without contravening anything we know from observation of nature, we may simply deny the scholastic axiom that two portions of matter cannot jointly occupy the same space, and may assert, as an admissible hypothesis, that ether does occupy the same space as ponderable matter, and that ether is not displaced by ponderable bodies moving through space occupied by ether. But how then could matter act on ether, and ether act on matter, to produce the known phenomena of light (or radiant heat), generated by the action of ponderable bodies on ether, and acting on ponderable bodies to produce its visual, chemical, phosphorescent, thermal, and photographic effects? There is no difficulty in answering this question if, as it probably is, ether is a compressible and dilatable * solid. We have only to suppose that the atom exerts force on the ether, by which condensation or rarefaction is produced within the space occupied by the atom. At present † I confine myself, for the sake of simplicity, to the suggestion of a spherical atom producing condensation and rarefaction, with concentric spherical surfaces of equal density, but the same total quantity of ether within its boundary as the quantity in an equal volume of free undisturbed ether.

§ 4. Consider now such an atom given at rest anywhere in space occupied by ether. Let force be applied to it to cause it to move in any direction, first with gradually increasing speed, and after that with uniform speed. If this speed is anything less than the velocity of light, the force may be mathematically proved to become zero at some short time after the instant when the velocity of the atom becomes uniform, and to remain zero for ever thereafter. What takes place is this:

§ 5. During all the time in which the velocity of the atom is being augmented from zero, two sets of non-periodic waves, one of them equi-voluminal, the other irrotational (which is therefore condensational-rarefactional), are being sent out in

* To deny this property is to attribute to ether infinitely great resistance against forces tending to condense it or to dilate it—which seems, in truth, an infinitely difficult assumption.

† Further developments of the suggested idea have been contributed to the Royal Society of Edinburgh, and to the Congrès International de Physique, held in Paris in August. (Proc. R.S.E. July 1900; vol. of reports, in French, of the Cong. Inter.; and Phil. Mag., Aug., Sept., 1900.)

all directions through the surrounding ether. The rears of the last of these waves leave the atom, at some time after its acceleration ceases. This time, if the motion of the ether outside the atom, close beside it, is infinitesimal, is equal to the time taken by the slower wave (which is the equi-voluminal) to travel the diameter of the atom, and is the short time referred to in § 4. When the rears of both waves have got clear of the atom, the ether within it and in the space around it, left clear by both rears, has come to a steady state of motion relatively to the atom. This steady motion approximates more and more nearly to uniform motion in parallel lines, at greater and greater distances from the atom. At a distance of twenty diameters it differs exceedingly little from uniformity.

§ 6. But it is only when the velocity of the atom is very small in comparison with the velocity of light, that the disturbance of the ether in the space close round the atom is infinitesimal. The propositions asserted in § 4 and the first sentence of § 5 are true, however little the final velocity of the atom falls short of the velocity of light. If this uniform final velocity of the atom exceeds the velocity of light, by ever so little, a non-periodic conical wave of equi-voluminal motion is produced, according to the same principle as that illustrated for sound by Mach's beautiful photographs of illumination by electric spark, showing, by changed refractivity, the condensational-rarefactional disturbance produced in air by the motion through it of a rifle bullet. The semi-vertical angle of the cone, whether in air or ether, is equal to the angle whose sine is the ratio of the wave velocity to the velocity of the moving body *.

* On the same principle we see that a body moving steadily (and, with little error, we may say also that a fish or water-fowl propelling itself by fins or web-feet) through calm water, either floating on the surface or wholly submerged at some moderate distance below the surface, produces no wave disturbance if its velocity is less than the minimum wave velocity due to gravity and surface tension (being about 23 cms. per second, or ·44 of a nautical mile per hour, whether for sea water or fresh water); and if its velocity exceeds the minimum wave velocity, it produces a wave disturbance bounded by two lines inclined on each side of its wake at angles each equal to the angle whose sine is the minimum wave velocity divided by the velocity of the moving body. It is easy for anyone to observe this by dipping vertically a pencil or a walking-stick into still water in a pond (or even in a good-sized hand basin), and moving it horizontally, first with exceeding small speed, and afterwards faster and faster. I first noticed it nineteen years ago, and described observations for an experimental determination of the minimum velocity of waves, in a letter to William Froude, published in 'Nature' for October 26, and in the Phil. Mag. for November 1871, from which the following is extracted. "[Recently, in the schooner yacht *Lalla*

§ 7. If, for a moment, we imagine the steady motion of the atom to be at a higher speed than the wave velocity of the condensational-rarefactional wave, two conical waves, of angles corresponding to the two wave velocities, will be steadily produced ; but we need not occupy ourselves at present with this case because the velocity of the condensational-rarefactional wave in ether is, we are compelled to believe, enormously great in comparison with the velocity of light.

§ 8. Let now a periodic force be applied to the atom so as to cause it to move to and fro continually, with simple harmonic motion. By the first sentence of § 5 we see that two sets of periodic waves, one equi-voluminal, the other irrotational, are continually produced. Without mathematical investigation we see that if, as in ether, the condensational-rarefactional wave velocity is very great in comparison with the equi-voluminal wave velocity, the energy taken by the condensational-rarefactional wave is exceedingly small in comparison with that taken by the equi-voluminal wave ; how small we can find easily enough by regular mathematical investigation. Thus we see how it is that the hypothesis of § 3 suffices for the answer suggested in that section to the question, How could matter act on ether so as to produce light ?

§ 9. But this, though of primary importance, is only a small part of the very general question pointed out in § 3 as needing answer. Another part, fundamental in the

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" *Rookh*], being becalmed in the Sound of Mull, I had an excellent " opportunity, with the assistance of Professor Helmholtz, and my " brother from Belfast [the late Professor James Thomson], of deter- " mining by observation the minimum wave-velocity with some approach " to accuracy. The fishing-line was hung at a distance of two or three " feet from the vessel's side, so as to cut the water at a point not sensibly " disturbed by the motion of the vessel. The speed was determined by " throwing into the sea pieces of paper previously wetted, and observing " their times of transit across parallel planes, at a distance of 912 centi- " metres asunder, fixed relatively to the vessel by marks on the deck and " gunwale. By watching carefully the pattern of ripples and waves which " connected the ripples in front with the waves in rear, I had seen that " it included a set of parallel waves slanting off obliquely on each side " and presenting appearances which proved them to be waves of the " critical length and corresponding minimum speed of propagation." When the speed of the yacht fell to but little above the critical velocity, the front of the ripples was very nearly perpendicular to the line of motion, and when it just fell below the critical velocity the ripples disappeared altogether, and there was no perceptible disturbance on the surface of the water. The sea was " glassy " ; though there was wind enough to propel the schooner at speed varying between $\frac{1}{4}$ mile and 1 mile per hour.

undulatory theory of optics, is, How is it that the velocity of light is smaller in transparent ponderable matter than in pure ether? Attention was called to this particular question in my address, to the Royal Institution, of last April; and a slight explanation of my proposal for answering it was given, and illustrated by a diagram. The validity of this proposal is confirmed by a somewhat elaborate discussion and mathematical investigation of the subject worked out since that time and communicated under the title, "On the Motion produced in an infinite Elastic Solid by the Motion through the Space occupied by it of a Body acting on it only by Attraction or Repulsion," to the Royal Society of Edinburgh on July 16, and to the Congrès International de Physique for its meeting at Paris in the beginning of August *.

§ 10. The other phenomena referred to in § 3 come naturally under the general dynamics of the undulatory theory of light, and the full explanation of them all is brought much nearer if we have a satisfactory fundamental relation between ether and matter, instead of the old intractable idea that atoms of matter displace ether from the space before them, when they are in motion relatively to the ether around them. May we then suppose that the hypothesis which I have suggested clears away the first of our two clouds? It certainly would explain the "aberration of light" connected with the earth's motion through ether in a thoroughly satisfactory manner. It would allow the earth to move with perfect freedom through space occupied by ether without displacing it. In passing through the earth the ether, an elastic solid, would not be lacerated as it would be according to Fresnel's idea of porosity and ether moving through the pores as if it were a fluid. Ether would move relatively to ponderables with the perfect freedom wanted for what we know of aberration, instead of the imperfect freedom of air moving through a grove of trees suggested by Thomas Young. According to it, and for simplicity neglecting the comparatively very small component due to the earth's rotation (only ·46 of a kilometre per second at the equator where it is a maximum), and neglecting the imperfectly known motion of the solar system through space towards the constellation Hercules, discovered by Herschel †,

* Phil. Mag., Aug. 1900.

† The splendid spectroscopic method originated by Huggins thirty-three years ago, for measuring the component in the line of vision of the relative motion of the earth, and any visible star, has been carried on since that time with admirable perseverance and skill by other observers, who have from their results made estimates of the velocity and direction of the motion through space of the centre of inertia of the solar system.

there would be at all points of the earth's surface a flow of ether at the rate of 30 kilometres per second in lines all parallel to the tangent to the earth's orbit round the sun. There is nothing inconsistent with this in all we know of the ordinary phenomena of terrestrial optics; but, alas! there is inconsistency with a conclusion that ether in the earth's atmosphere is motionless relatively to the earth, seemingly proved by an admirable experiment designed by Michelsen, and carried out, with most searching care to secure a trustworthy result, by himself and Morley *. I cannot see any flaw either in the idea or in the execution of this experiment. But a possibility of escaping from the conclusion which it seemed to prove, may be found in a brilliant suggestion made independently by FitzGerald † and by Lorentz ‡ of Leyden, to the effect that the motion of ether through matter may slightly alter its linear dimensions, according to which if the stone slab constituting the sole plate of Michelsen and Morley's apparatus has, in virtue of its motion through space occupied by ether, its lineal dimensions shortened one one-hundred-millionth § in the direction of motion, the result of the experiment would not disprove the free motion of ether through space occupied by the earth.

§ 11. I am afraid we must still regard Cloud No. I. as very dense.

§ 12. Cloud II.—Waterston (in a communication to the Royal Society, now famous; which, after lying forty-five years buried and almost forgotten in the archives, was

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My Glasgow colleague, Professor Becker, has kindly given me the following information on the subject of these researches:

"The early (1888) Potsdam photographs of the spectra of 51 stars brighter than $2\frac{1}{2}$ magnitude have been employed for the determination of the apex and velocity of the solar system. Kempf (*Astronomische Nachrichten*, vol. 132) finds for the apex: right ascension, $206^\circ \pm 12^\circ$; declination, $46^\circ \pm 9^\circ$; velocity, 19 kilometres per second; and Risteen (Astronomical Journal, 1893) finds practically the same quantities. The proper motions of the fixed stars assign to the apex a position which may be anywhere in a narrow zone parallel to the Milky-way, and extending 20° on both sides of a point of Right Ascension 275° and Declination $+30^\circ$. The authentic mean of 13 values determined by the methods of Argelander or Airy gives 274° and $+35^\circ$ (André, *Traité d' Astronomie Stellaire*)."

* Phil. Mag., December 1887.

† Public Lectures in Trinity College, Dublin.

‡ *Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern.*

§ This being the square of the ratio of the earth's velocity round the sun (30 kilometres per sec.) to the velocity of light (300,000 kilometres per sec.).

rescued from oblivion by Lord Rayleigh and published, with an introductory notice of great interest and importance, in the Transactions of the Royal Society for 1892), enunciated the following proposition: "In mixed media the mean square "molecular velocity is inversely proportional to the specific "weight of the molecule. This is the law of the equilibrium "of vis viva." Of this proposition Lord Rayleigh in a footnote * says, "This is the first statement of a very "important theorem (see also Brit. Assoc. Rep., 1851). "The demonstration, however, of § 10 can hardly be de- "fended. It bears some resemblance to an argument "indicated and exposed by Professor Tait (Edinburgh "Trans., vol. 33, p. 79, 1886). There is reason to think "that this law is intimately connected with the Maxwellian "distribution of velocities of which Waterston had no know- "ledge."

§ 13. In Waterston's statement, the "specific weight of a molecule" means what we now call simply the mass of a molecule; and "molecular velocity" means the translational velocity of a molecule. Writing on the theory of sound in the Phil. Mag. for 1858, and referring to the theory developed in his buried paper †, Waterston said, "The theory ". . . . assumes . . . . that if the impacts produce rotatory "motion the vis viva thus invested bears a constant ratio to "the rectilineal vis viva." This agrees with the very important principle or truism given independently about the same time by Clausius to the effect that the mean energy, kinetic and potential, due to the relative motion of all the parts of any molecule of a gas, bears a constant ratio to the mean energy of the motion of its centre of inertia when the density and pressure are constant.

§ 14. Without any knowledge of what was to be found in Waterston's buried paper, Maxwell, at the meeting of the British Association at Aberdeen, in 1859 ‡ gave the following proposition regarding the motion and collisions of perfectly elastic spheres: "Two systems of particles move in the same "vessel; to prove that the mean vis viva of each particle "will become the same in the two systems." This is precisely Waterston's proposition regarding the law of partition of energy, quoted in § 12 above; but Maxwell's 1860 proof was certainly not more successful than Waterston's. Max-

* Phil. Trans. A, 1892, p. 16.

† "On the Physics of Media that are composed of Force and Perfectly Elastic Molecules in a State of Motion." Phil. Trans., A, 1892, p. 13.

‡ "Illustrations of the Dynamical Theory of Gases," Phil. Mag., January and July 1860, and collected works, vol. i. p. 378.

well's 1860 proof has always seemed to me quite inconclusive, and many times I urged my colleague, Professor Tait, to enter on the subject. This he did, and in 1886 he communicated to the Royal Society of Edinburgh a paper * on the foundations of the kinetic theory of gases, which contained a critical examination of Maxwell's 1860 paper, highly appreciative of the great originality and splendid value, for the kinetic theory of gases, of the ideas and principles set forth in it; but showing that the demonstration of the theorem of the partition of energy in a mixed assemblage of particles of different masses was inconclusive, and successfully substituting for it a conclusive demonstration.

§ 15. Waterston, Maxwell, and Tait, all assume that the particles of the two systems are thoroughly mixed (Tait, § 18), and their theorem is of fundamental importance in respect to the specific heats of mixed gases. But they do not, in any of the papers already referred to, give any indication of a proof of the corresponding theorem, regarding the partition of energy between two sets of equal particles separated by a membrane impermeable to the molecules, while permitting forces to act across it between the molecules on its two sides †, which is the simplest illustration of the molecular dynamics of Avogadro's law. It seems to me, however, that Tait's demonstration of the Waterston-Maxwell law may possibly be shown to virtually include, not only this vitally important subject, but also the very interesting, though comparatively unimportant, case of an assemblage of particles of equal masses with a single particle of different mass moving about among them.

§ 16. In §§ 12, 14, 15, "particle" has been taken to mean what is commonly, not correctly, called an elastic sphere, but what is in reality a Boscovich atom acting on other atoms in lines exactly through its centre of inertia (so that no rotation is in any case produced by collisions), with, as law of action between two atoms, *no force at distance greater than the sum of their radii, infinite force at exactly this distance.* None of the demonstrations, unsuccessful or successful, to which I have referred would be essentially altered if, instead of this last condition, we substitute a repulsion increasing with

* Phil. Trans. R.S.E., "On the Foundations of the Kinetic Theory of Gases," May 14 and December 6, 1886, and January 7, 1887. (Abstract in Phil. Mag. April 1886 and Feb. 1887.)

† A very interesting statement is given by Maxwell regarding this subject in his latest paper regarding the Boltzmann-Maxwell doctrine. "On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points," Camb. Phil. Trans., May 6, 1878; Collected Works, vol. ii. pp. 713–741.

diminishing distance, according to any law for distances less than the sum of the radii, subject only to the condition that it would be infinite before the distance became zero. In fact the impact, oblique or direct, between two Boscovich atoms thus defined, has the same result after the collision is completed (that is to say, when their spheres of action get outside one another) as collision between two conventional elastic spheres, imagined to have radii dependent on the lines and velocities of approach before collision (the greater the relative velocity the smaller the effective radii); and the only assumption essentially involved in those demonstrations is, that the radius of each sphere is very small in comparison with the average length of free path.

§ 17. But if the particles are Boscovich atoms, having centre of inertia not coinciding with centre of force; or quasi Boscovich atoms, of non-spherical figure; or (a more acceptable supposition) if each particle is a cluster of two or more Boscovich atoms: rotations and changes of rotation would result from collisions. Waterston's and Clausius' leading principle, quoted in § 13 above, must now be taken into account, and Tait's demonstration is no longer applicable. Waterston and Clausius, in respect to rotation, both wisely abstained from saying more than that the average kinetic energy of rotation bears a constant ratio to the average kinetic energy of translation. With magnificent boldness Boltzmann and Maxwell declared that the ratio is equality; Boltzmann having found what seemed to him a demonstration of this remarkable proposition, and Maxwell having accepted the supposed demonstration as valid.

§ 18. Boltzmann went further * and extended the theorem of equality of mean kinetic energies to any system of a finite number of material points (Boscovich atoms) acting on one another, according to any law of force, and moving freely among one another; and finally, Maxwell † gave a demonstration extending it to the generalized Lagrangian co-ordinates of any system whatever, with a finite or infinitely great number of degrees of freedom. The words in which he enunciated his supposed theorem are as follows:

"The only assumption which is necessary for the direct "proof is that the system, if left to itself in its actual state of

* "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten." *Sitzb. K. Akad. Wien*, October 8, 1868.

† "On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points." Maxwell's Collected Papers, vol. ii. pp. 713–741, and Camb. Phil. Trans., May 6, 1878.

"motion, will, sooner or later, pass [infinitely nearly *] "through every phase which is consistent with the equation "of energy" (p. 714) and, again (p. 716).

"It appears from the theorem, that in the ultimate state of "the system the average † kinetic energy of two portions "of the system must be in the ratio of the number of degrees "of freedom of those portions.

"This, therefore, must be the condition of the equality of "temperature of the two portions of the system."

I have never seen validity in the demonstration ‡ on which Maxwell founds this statement, and it has always seemed to me exceedingly improbable that it can be true. If true, it would be very wonderful, and most interesting in pure mathematical dynamics. Having been published by Boltzmann and Maxwell it would be worthy of most serious attention, even without consideration of its bearing on thermo-dynamics. But, when we consider its bearing on thermo-dynamics, and in its first and most obvious application we find it destructive of the kinetic theory of gases, of which Maxwell was one of the chief founders, we cannot see it otherwise than as a cloud on the dynamical theory of heat and light.

§ 19. For the kinetic theory of gases, let each molecule be a cluster of Boscovich atoms. This includes every possibility ("dynamical," or "electrical," or "physical," or "chemical") regarding the nature and qualities of a molecule and of all its parts. The mutual forces between the constituent atoms must be such that the cluster is in stable equilibrium if given at rest; which means, that if started from equilibrium with

* I have inserted these two words as certainly belonging to Maxwell's meaning.—K.

† The average here meant is a time-average through a sufficiently long time.

‡ The mode of proof followed by Maxwell, and its connection with antecedent considerations of his own and of Boltzmann, imply, as included in the general theorem, that the average kinetic energy of any one of three rectangular components of the motion of the centre of inertia of an isolated system, acted upon only by mutual forces between its parts, is equal to the average kinetic energy of each generalized component of motion relatively to the centre of inertia. Consider, for example, as "parts of the system" two particles of masses m and m' free to move only in a fixed straight line, and connected to one another by a massless spring. The Boltzmann-Maxwell doctrine asserts that the average kinetic energy of the motion of the inertial centre is equal to the average kinetic energy of the motion relative to the inertial centre. This is included in the wording of Maxwell's statement in the text if, but not unless, $m=m'$. See footnote on § 7 of my paper "On some Test-Cases for the Boltzmann-Maxwell Doctrine regarding Distribution of Energy." Proc. Roy. Soc., June 11, 1891.

its constituents in any state of relative motion, no atom will fly away from it, provided the total kinetic energy of the given initial motion does not exceed some definite limit. A gas is a vast assemblage of molecules thus defined, each moving freely through space, except when in collision with another cluster, and each retaining all its own constituents unaltered, or only altered by interchange of similar atoms between two clusters in collision.

§ 20. For simplicity we may suppose that each atom, A, has a definite radius of activity, α, and that atoms of different kinds, A, A′, have different radii of activity, α, α'; such that A exercises no force on any other atom, A′, A″, when the distance between their centres is greater than $\alpha+\alpha'$ or $\alpha+\alpha''$. We need not perplex our minds with the inconceivable idea of "virtue," whether for force or for inertia, residing in a mathematical point* the centre of the atom; and without mental strain we can distinctly believe that the substance (the "substratum" of qualities) resides, not in a point, nor vaguely through all space, but definitely in the spherical volume of space bounded by the spherical surface whose radius is the radius of activity of the atom, and whose centre is the centre of the atom. In our intermolecular forces thus defined, we have no violation of the old scholastic law, "Matter cannot act where it is not," but we explicitly violate the other scholastic law, "Two portions of matter cannot simultaneously occupy the same space." We leave to gravitation, and possibly to electricity (probably not to magnetism), the at present very unpopular idea of action at a distance.

§ 21. We need not now (as in § 16, when we wished to keep as near as we could to the old idea of colliding elastic globes) suppose the mutual force to become infinite repulsion before the centres of two atoms, approaching one another, meet. Following Boscovich, we may assume the force to vary according to any law of alternate attraction and repulsion, but without supposing any infinitely great force, whether of repulsion or attraction, at any particular distance; but we must assume the force to be zero when the centres are coincident. We may even admit the idea of the centres being absolutely coincident, in at all events some cases of a chemical combination of two or more atoms; although we might consider it more probable that in most cases the chemical combination is a cluster, in which the volumes of the constituent atoms overlap without any two centres absolutely coinciding.

§ 22. The word "collision" used without definition in § 19 may now, in virtue of §§ 20, 21, be unambiguously defined

* See Math. and Phys. Papers, vol. iii. art. XCVII. "Molecular Constitution of Matter," § 14.

thus: Two atoms are said to be in collision during all the time their volumes overlap after coming into contact. They necessarily in virtue of inertia separate again, unless some third body intervenes with action which causes them to remain overlapping; that is to say, causes combination to result from collision. Two clusters of atoms are said to be in collision when, after being separate, some atom or atoms of one cluster come to overlap some atom or atoms of the other. In virtue of inertia the collision must be followed either by the two clusters separating, as described in the last sentence of § 19, or by some atom or atoms of one or both systems being sent flying away. This last supposition is a matter-of-fact statement belonging to the magnificent theory of dissociation, discovered and worked out by Sainte-Clair Deville without any guidance from the kinetic theory of gases. In gases approximately fulfilling the gaseous laws (Boyle's and Charles'), two clusters must in general fly asunder after collision. Two clusters could not possibly remain permanently in combination without at least one atom being sent flying away after collision between two clusters with no third body intervening *.

§ 23. Now for the application of the Boltzmann-Maxwell doctrine to the kinetic theory of gases: consider first a homogeneous single gas, that is, a vast assemblage of similar clusters of atoms moving and colliding as described in the last sentence of § 19; the assemblage being so sparse that the time during which each cluster is in collision is very short in comparison with the time during which it is unacted on by other clusters, and its centre of inertia, therefore, moves uniformly in a straight line. If there are i atoms in each cluster, it has $3i$ freedoms to move, that is to say, freedoms in three rectangular directions for each atom. The Boltzmann-Maxwell doctrine asserts that the mean kinetic energies of these $3i$ motions are all equal, whatever be the mutual forces between the atoms. From this, when the durations of the collisions are not included in the time-averages, it is easy to prove algebraically (with exceptions noted below) that the time-average of the kinetic energy of the component translational velocity of the inertial centre †, in any direction, is equal to any one of the $3i$ mean kinetic energies asserted to be equal to one another in the preceding statement. There are exceptions to the algebraic proof

* See Kelvin's Math. and Phys. Papers, vol. iii. Art. XCVII. § 33. In this reference, for "scarcely" substitute "not."

† This expression I use for brevity to signify the kinetic energy of the whole mass ideally collected at the centre of inertia.

corresponding to the particular exception referred to in the last footnote to § 18 above; but, nevertheless, the general Boltzmann-Maxwell doctrine includes the proposition, even in those cases in which it is not deducible algebraically from the equality of the $3i$ energies. Thus, without exception, the average kinetic energy of any component of the motion of the inertial centre is, according to the Boltzmann-Maxwell doctrine, equal to $\frac{1}{3i}$ of the whole average kinetic energy of the system. This makes the total average energy, potential and kinetic, of the whole motion of the system, translational and relative, to be $3i(1+\mathrm{P})$ times the mean kinetic energy of one component of the motion of the inertial centre, where P denotes the ratio of the mean potential energy of the relative displacements of the parts to the mean kinetic energy of the whole system. Now, according to Clausius' splendid and easily proved theorem regarding the partition of energy in the kinetic theory of gases, the ratio of the difference between the two thermal capacities to the constant-volume thermal capacity is equal to the ratio of twice a single component of the translational energy to the total energy. Hence, if according to our usual notation we denote the ratio of the thermal capacity, pressure constant, to the thermal capacity, volume constant, by k, we have,

$$k - 1 = \frac{2}{3i(1+\mathrm{P})}.$$

§ 24. *Example* 1.—For first and simplest example, consider a monatomic gas. We have $i=1$, and according to our supposition (the supposition generally, perhaps universally, made) regarding atoms, we have $\mathrm{P}=0$. Hence, $k-1=\frac{2}{3}$.

This is merely a fundamental theorem in the kinetic theory of gases for the case of no rotational or vibrational energy of the molecule; in which there is no scope either for Clausius' theorem or for the Boltzmann-Maxwell doctrine. It is beautifully illustrated by mercury vapour, a monatomic gas according to chemists, for which many years ago Kundt, in an admirably designed experiment, found $k-1$ to be very approximately $\frac{2}{3}$; and by the newly discovered gases argon, helium, and krypton, for which also $k-1$ has been found to have approximately the same value, by Rayleigh and Ramsay. But each of these four gases has a large number of spectrum lines, and therefore a large number of vibrational freedoms, and therefore, if the Boltzmann-Maxwell doctrine were true, $k-1$ would have some exceedingly small value, such as that shown in the ideal example of § 26 below. On the other hand, Clausius' *theorem* presents no difficulty; it merely asserts that $k-1$ is necessarily less than $\frac{2}{3}$ in each of these four cases, as in every case in which there is any rotational or vibrational energy whatever; and proves, from the values found experimentally for $k-1$ in the four gases, that in each case the total of rotational and vibrational energy is exceedingly small in comparison with the translational energy. It justifies admirably the chemical doctrine that mercury vapour is *practically a monatomic gas*, and it proves that argon, helium, and krypton, are also *practically monatomic*, though none of these gases has hitherto shown any chemical affinity or action of any kind from which chemists could draw any such conclusion.

But Clausius' theorem, taken in connection with Stokes' and Kirchhoff's dynamics of spectrum analysis, throws a new light on what we are now calling a "practically monatomic gas." It shows that, unless we admit that the atom can be set into rotation or vibration by mutual collisions (a most unacceptable hypothesis), it must have satellites connected with it (or ether condensed into it or around it) and kept, by the collisions, in motion relatively to it with total energy exceedingly small in comparison with the translational energy of the whole system of atom and satellites. The satellites must in all probability be of exceedingly small mass in comparison with that of the chief atom. Can they be the "ions" by which J. J. Thomson explains the electric conductivity induced in air and other gases by ultra-violet light, Röntgen rays, and Becquerel rays?

Finally, it is interesting to remark that all the values of $k-1$ found by Rayleigh and Ramsay are somewhat less than $\frac{2}{3}$; argon ·64, ·61; helium ·652; krypton ·666. If the deviation from ·667 were accidental they would probably have been some in defect and some in excess.

Example 2.—As a next simplest example let $i=2$, and as a very simplest case let the two atoms be in stable equilibrium when concentric, and be infinitely nearly concentric when the clusters move about, constituting a homogeneous gas. This supposition makes $P=\frac{1}{2}$, because the average potential energy is equal to the average kinetic energy in simple harmonic vibrations; and in our present case half the whole kinetic energy, according to the Boltzmann-Maxwell doctrine, is vibrational, the other half being translational. We find $k-1=\frac{2}{9}=·2222$.

Example 3.—Let $i=2$; let there be stable equilibrium, with the centres C, C′ of the two atoms at a finite distance a

asunder, and let the atoms be always very nearly at this distance asunder when the clusters are not in collision. The relative motions of the two atoms will be according to three freedoms, one vibrational, consisting of very small shortenings and lengthenings of the distance C C′, and two rotational, consisting of rotations round one or other of two lines perpendicular to each other and perpendicular to C C′ through the inertial centre. With these conditions and limitations, and with the supposition that half the average kinetic energy of the rotation is comparable with the average kinetic energy of the vibrations, or exactly equal to it as according to the Boltzmann-Maxwell doctrine, it is easily proved that in rotation the excess of C C′ above the equilibrium distance a, due to centrifugal force, must be exceedingly small in comparison with the maximum value of $CC'-a$ due to the vibration. Hence the average potential energy of the rotation is negligible in comparison with the potential energy of the vibration. Hence, of the three freedoms for relative motion there is only one contributory to P, and therefore we have $P=\frac{1}{6}$. Thus we find $k-1=\frac{2}{7}=\cdot 2857$.

The best way of experimentally determining the ratio of the two thermal capacities for any gas is by comparison between the observed and the Newtonian velocities of sound. It has thus been ascertained that, at ordinary temperatures and pressures, $k-1$ differs but little from ·406 for common air, which is a mixture of the two gases nitrogen and oxygen, each diatomic according to modern chemical theory; and the greatest value that the Boltzmann-Maxwell doctrine can give for a diatomic gas is the ·2857 of Ex. 3. This notable discrepance from observation suffices to absolutely disprove the Boltzmann-Maxwell doctrine. What is really established in respect to partition of energy is what Clausius' theorem tells us (§ 23 above). We find, as a result of observation and true theory, that the average kinetic energy of translation of the molecules of common air is ·609 of the total energy, potential and kinetic, of the relative motion of the constituents of the molecules.

§ 25. The method of treatment of Ex. 3 above, carried out for a cluster of any number of atoms greater than two not in one line, $j+2$ atoms, let us say, shows us that there are three translational freedoms; three rotational freedoms, relatively to axes through the inertial centre; and $3j$ vibrational freedoms. Hence we have $P=\frac{j}{j+2}$, and we find $k-1=\frac{1}{3(1+j)}$. The values of $k-1$ thus calculated for a triatomic and tetratomic gas, and calculated as above in Ex. 3 for a diatomic gas, are shown in the following table, and compared with the results of observation for several such gases:

Gas.	Values of $k-1$.	
	According to the B.-M. doctrine.	By Observation.
Air	$\frac{2}{7} = \cdot 2857$	·406
H_2	,, ,,	·40
O_2	,, ,,	·41
Cl_2	,, ,,	·32
CO	,, ,,	·39
NO	,, ,,	·39
CO_2	$\frac{1}{6} = \cdot 1667$	·30
N_2O	,, ,,	·331
NH_3	$\frac{1}{9} = \cdot 1111$	·311

It is interesting to see how the dynamics of Clausius' theorem is verified by the results of observation shown in the table. The values of $k-1$ for all the gases are less than $\frac{2}{3}$, as they must be when there is any appreciable energy of rotation or vibration in the molecule. They are different for different diatomic gases; ranging from ·41 for oxygen to ·32 for chlorine, which is quite as might be expected, when we consider that the laws of force between the two atoms may differ largely for the different kinds of atoms. The values of $k-1$ are, on the whole, smaller for the tetratomic and triatomic than for the diatomic gases, as might be expected from consideration of Clausius' principle. It is probable that the differences of $k-1$ for the different diatomic gases are real, although there is considerable uncertainty with regard to the observational results for all or some of the gases other than air. It is certain that the discrepancies from the values, calculated according to the Boltzmann-Maxwell doctrine, are real and great; and that in each case, diatomic, triatomic, and tetratomic, the doctrine gives a value for $k-1$ much smaller than the truth.

§ 26. But, in reality, the Boltzmann-Maxwell doctrine errs enormously more than is shown in the preceding table. Spectrum analysis showing vast numbers of lines for each gas makes it certain that the numbers of freedoms of the constituents of each molecule is enormously greater than those which we have been counting, and therefore that unless we attribute vibratile quality to each individual atom, the molecule of every one of the ordinary gases must have a vastly greater number of atoms in its constitution than those hitherto reckoned in regular chemical doctrine. Suppose, for example, there are forty-one atoms in the molecule of any particular gas; if the doctrine were true, we should have $j=39$. Hence there are 117 vibrational freedoms, so that there might be 117 visible lines in the spectrum of the gas; and we have $k-1=\frac{1}{120}=\cdot 0083$. There is, in fact, no possibility of reconciling the Boltzmann-Maxwell doctrine with the truth regarding the specific heats of gases.

§ 27. It is, however, not quite possible to rest contented with the mathematical verdict not proven, and the experimental verdict not true, in respect to the Boltzmann-Maxwell doctrine. I have always felt that it should be mathematically tested by the consideration of some particular case. Even if the theorem were true, stated as it was somewhat vaguely, and in such general terms that great difficulty has been felt as to what it is really meant to express, it would be very desirable to see even one other simple case, besides that original one of Waterston's, clearly stated and tested by pure mathematics. Ten years ago *, I suggested a number of test-cases, some of which have been courteously considered by Boltzmann; but no demonstration either of the truth or untruth of the doctrine as applied to any one of them has hitherto been given. A year later, I suggested what seemed to me a decisive test-case disproving the doctrine; but my statement was quickly and justly criticised by Boltzmann and Poincaré; and more recently Lord Rayleigh † has shown very clearly that my simple test-case was quite indecisive. This last article of Rayleigh's has led me to resume the consideration of several classes of dynamical problems, which had occupied me more or less at various times during the last twenty years, each presenting exceedingly interesting features in connection with the double question: Is this a case which admits of the application of the Boltzmann-Maxwell doctrine; and if so, is the doctrine true for it?

§ 28. Premising that the mean kinetic energies with which the Boltzmann-Maxwell doctrine is concerned are time-integrals of energies divided by totals of the times, we may conveniently divide the whole class of problems, with

* 'On some Test Cases for the Maxwell-Boltzmann Doctrine regarding Distribution of Energy.' Proc. Roy. Soc., June 11, 1891.

† Phil. Mag., vol. xxxiii. 1892, p. 356. "Remarks on Maxwell's Investigation respecting Boltzmann's Theorem."

reference to which the doctrine comes into question, into two classes.

Class I. Those in which the velocities considered are either constant or only vary suddenly—that is to say, in infinitely small times—or in times so short that they may be omitted from the time-integration. To this class belong:

(*a*) The original Waterston-Maxwell case and the collisions of ideal rigid bodies of any shape, according to the assumed law that the translatory and rotatory motions lose no energy in the collisions.

(*b*) The frictionless motion of one or more particles constrained to remain on a surface of any shape, this surface being either closed (commonly called finite though really endless), or being a finite area of plane or curved surface, bounded like a billiard-table, by a wall or walls, from which impinging particles are reflected at angles equal to the angles of incidence.

(*c*) A closed surface, with non-vibratory particles moving within it freely except during impacts of particles against one another or against the bounding surface.

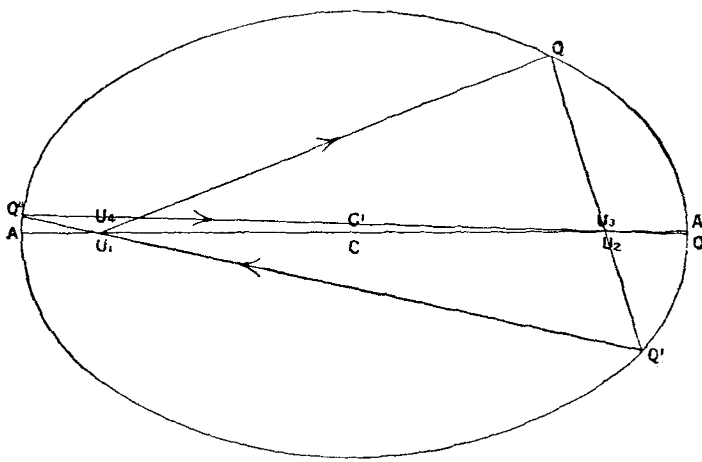
(*d*) Cases such as (*a*), (*b*), or (*c*), with impacts against boundaries and mutual impacts between particles, softened by the supposition of finite forces during the impacts, with only the condition that the durations of the impacts are so short as to be practically negligible in comparison with the durations of free paths.

Class II. Cases in which the velocities of some of the particles concerned sometimes vary gradually; so gradually that the times during which they vary must be included in the time-integration. To this class belong examples such as (*d*) of Class I. with durations of impacts not negligible in the time-integration.

§ 29. Consider first Class I. (*b*) with a finite closed surface as the field of motion and a single particle moving on it. If a particle is given, moving in any direction through any point I of the field, it will go on for ever along one determinate geodetic line. The question that first occurs is, Does the motion fulfil Maxwell's condition (see § 18 above)? that is to say, for this case, If we go along the geodetic line long enough, shall we pass infinitely nearly to any point Q whatever, including I, of the surface an infinitely great number of times in all directions? This question cannot be answered in the affirmative without reservation. For example, if the surface be exactly an ellipsoid it must be answered in the negative, as is proved in the following §§ 30, 31, 32.

§ 30. Let AA′, BB′, CC′, be the ends of the greatest, mean, and least diameters of an ellipsoid. Let U_1 U_2 U_3 U_4 be the umbilics in the arcs AC, CA′, A′C′, C′A. A known theorem in the geometry of the ellipsoid tells us, that every geodetic through U_1 passes through U_3, and every geodetic through U_2 passes through U_4. This statement regarding geodetic lines on an ellipsoid of three unequal axes is illustrated by fig. 1, a diagram showing for the extreme case in which the shortest axis is zero, the exact construction of a geodetic through U_1 which is a focus of the ellipse shown in the diagram. U_3, C′, U_4 being infinitely near to U_2, C, U_1 respectively are indicated by double letters at the same points. Starting from U_1 draw the geodetic U_1QU_3; the two parts

Fig. 1.

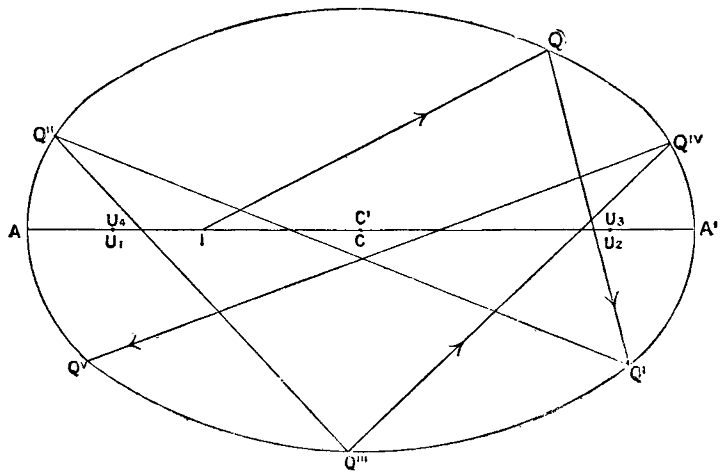


of which U_1Q and QU_3 are straight lines. It is interesting to remark that, in whatever direction we start from U_1, if we continue the geodetic through U_3, and on through U_1 again and so on endlessly, as indicated in the diagram by the straight lines $U_1QU_3Q'U_1Q''U_3Q'''$, and so on, we come very quickly to lines approaching successively more and more nearly to coincidence with the major axis. At every point where the path strikes the ellipse it is reflected at equal angles to the tangent. The construction is most easily made by making the angle between the reflected path and a line to one focus, equal to the angle between the incident path and a line to the other focus.

§ 31. Returning now to the ellipsoid :—From any point I, between U_1 and U_2, draw the geodetic IQ, and produce it through Q on the ellipsoidal surface. It must cut the arc A′C′A at some point between U_3 and U_4, and, if continued on and on, it must cut the ellipse ACA′C′A successively between U_1 and U_2, or between U_3 and U_4; never between U_2 and U_3, or U_4 and U_1. This, for the extreme case of the smallest axis zero, is illustrated by the path IQQ′Q″Q‴ $Q^{iv}Q^{v}$ in fig. 2.

§ 32. If now, on the other hand, we commence a geodetic through any point J between U_1 and U_4, or between U_2 and U_3, it will never cut the principal section containing the umbilicus, either between U_1 and U_2 or between U_3 and U_4. This, for the extreme case of $CC'=0$, is illustrated in fig. 3.

Fig. 2.

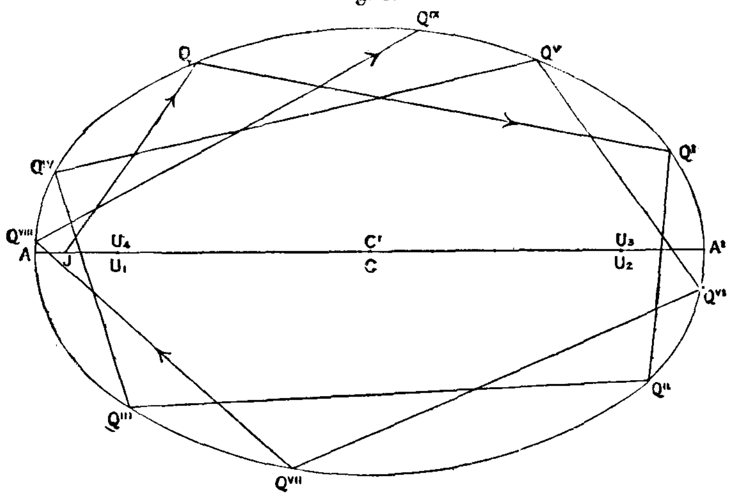


§ 33. It seems not improbable that if the figure deviates by ever so little from being exactly ellipsoidal, Maxwell's condition might be fulfilled. It seems indeed quite probable that Maxwell's condition (see §§ 13, 29, above) is fulfilled by a geodetic on a closed surface of any shape in general, and that exceptional cases, in which the question of § 29 is to be answered in the negative, are merely particular surfaces of definite shapes, infinitesimal deviations from which will allow the question to be answered in the affirmative.

§ 34. Now with an affirmative answer to the question—is Maxwell's condition fulfilled?—what does the Boltzmann-Maxwell doctrine assert in respect to a geodetic on a closed surface? The mere wording of Maxwell's statement, quoted in §13 above, is not applicable to this case, but the meaning of the doctrine as interpreted from previous writings both of Boltzmann and Maxwell, and subsequent writings of Boltzmann, and of Rayleigh *, the most recent supporter of the doctrine, is that a single geodetic drawn long enough will not only fulfil Maxwell's condition of passing infinitely near to every point of the surface in all directions, but will pass with equal frequencies in all directions; and as many times within a certain infinitesimal distance $\pm\delta$ of any one point P as of any other point P′ anywhere over the whole surface. This, if true, would be an exceedingly interesting theorem.

§ 35. I have made many efforts to test it for the case in which the closed surface is reduced to a plane with other boundaries than an exact ellipse (for which, as we have seen

Fig. 3.

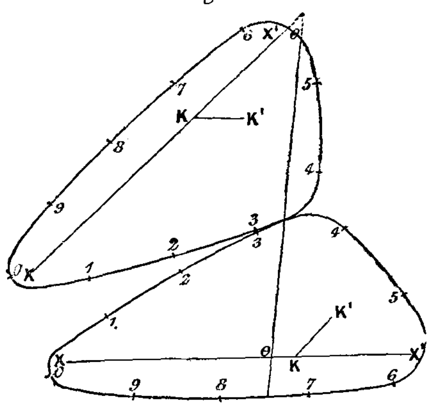


in §§ 30, 31, 32, the investigation fails through the non-fulfilment of Maxwell's preliminary condition). Every such case gives, as we have seen, straight lines drawn across the enclosed area turned on meeting the boundary, according to the law of equal angles of incidence and reflection, which corresponds also to the case of an ideal perfectly smooth non-rotating billiard-ball moving in straight lines except when it strikes the boundary of the table; the boundary being of any shape whatever, instead of the ordinary rectangular boundary of an ordinary billiard-table, and being perfectly elastic. An interesting illustration, easily seen

* Phil. Mag., January 1900.

through a large lecture-hall, is had by taking a thin wooden board, cut to any chosen shape, with the corner edges of the boundary smoothly rounded, and winding a stout black cord round and round it many times, beginning with one end fixed to any point, I, of the board. If the pressure of the cord on the edges were perfectly frictionless, the cord would, at every turn round the border, place itself so as to fulfil the law of equal angles of incidence and reflection, modified in virtue of the thickness of the board. For stability, it would be necessary to fix points of the cord to the board by staples pushed in over it at sufficiently frequent intervals, care being taken that at no point is the cord disturbed from its proper straight line by the staple. [Boards of a considerable variety

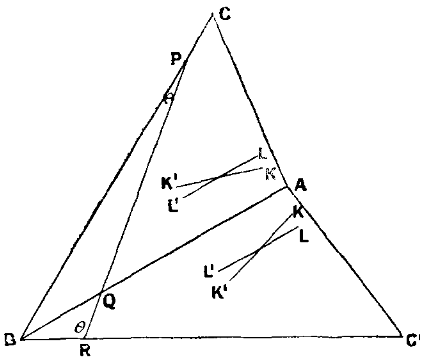
Fig. 4.



of shape with cords thus wound on them were shown as illustrations of the lecture.]

§ 36. A very easy way of drawing accurately the path of a particle moving in a plane and reflected from a bounding wall of any shape, provided only that it is not concave externally in any part, is furnished by a somewhat interesting kinematical method illustrated by the accompanying diagram (fig. 4). It is easily realized by using two equal and similar pieces of board, cut to any desired figure, one of them being turned upside down relatively to the other, so that when the two are placed together with corresponding points in contact, each is the image of the other relative to the plane of contact regarded as a mirror. Sufficiently close corresponding points should be accurately marked on the boundaries of the two figures, and this allows great accuracy to be obtained in the drawing of the free path after each reflection. The diagram shows consecutive free paths 74·6—32·9 given, and 32·9—54·7, found by producing 74·6—32·9 through the point of contact. The process involves the exact measurement of the length (l)—say to three significant figures—and its inclination (θ) to a chosen line of reference XX′. The summations $\Sigma\ l \cos 2\theta$ and $\Sigma\ l \sin 2\theta$ give, as explained below, the difference of time-integrals of kinetic energies of component motions parallel and perpendicular respectively to XX′, and parallel and perpendicular respectively to KK′, inclined at 45° to XX′. From these differences we find (by a procedure equivalent to that of finding the principal axes of an ellipse) two lines at right angles to one another, such that the time-integrals of the components of velocity parallel to

Fig. 5.



them are respectively greater than and less than those of the components parallel to any other line. [This process was illustrated by models in the lecture.]

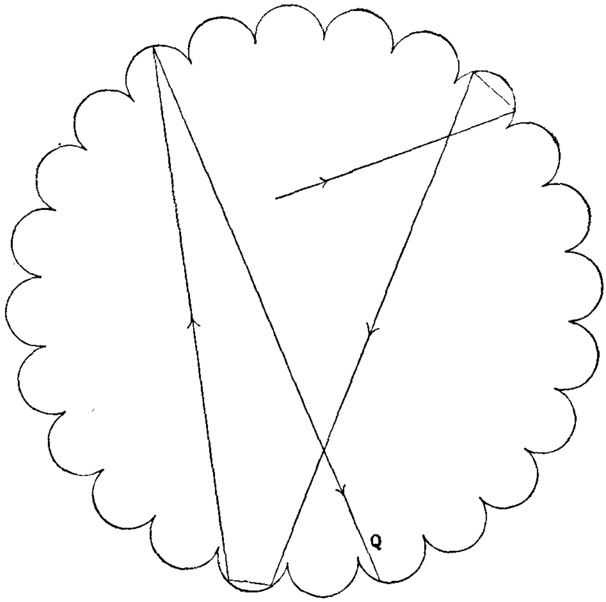
§ 37. Virtually the same process as this, applied to the case of a scalene triangle ABC (in which BC=20 centimetres and the angles A=97°, B=29°·5, C=53°·5), was worked out in the Royal Institution during the fortnight after the lecture, by Mr. Anderson, with very interesting results. The length of each free path (l), and its inclination to BC (θ), reckoned acute or obtuse according to the indications in the diagram (fig. 5), were measured to the nearest millimetre and the nearest integral degree. The first free path was drawn at random, and the continuation, through 599 reflections (in all 600 paths), was drawn in a manner illustrated by fig. 5, which shows, for example, a path PQ on one triangle continued to QR on the other. The two when folded together round the line AB show a path PQ, continued on QR after reflection. For each path $l\cos 2\theta$ and $l\sin 2\theta$ were calculated and entered in tables with the proper algebraic signs. Thus, for the whole 600 paths, the following summations were found :—

$$\Sigma l = 3298;\ \Sigma l\cos 2\theta = +128{\cdot}8;\ \Sigma l\sin 2\theta = -201{\cdot}9.$$

Remark, now, if the mass of the moving particle is 2, and the velocity one centimetre per second, $\Sigma l\cos 2\theta$ is the excess of the time-integral of kinetic energy of component motion parallel to BC above that of component motion perpendicular to BC, and $\Sigma\, l\sin 2\theta$ is the excess of the time-integral of kinetic energy of component motion perpendicular to KK′ above that of component motion parallel to KK′; KK′ being inclined at 45° to BC in the direction shown in the diagram. Hence the positive value of $\Sigma l\cos 2\theta$ indicates a preponderance of kinetic energy due to component motion parallel to BC above that of component motion perpendicular to BC; and the negative sign of $\Sigma l\sin 2\theta$ shows preponderance of kinetic energy of component motion parallel to KK′, above that of component motion perpendicular to KK′. Deducing a determination of two axes at right angles to each other, corresponding respectively to maximum and minimum kinetic energies, we find that LL′, being inclined to KK′ in the direction shown, at an angle $= \frac{1}{2}\tan^{-1}\frac{128{\cdot}8}{201{\cdot}9}$, is what we may call the axis of maximum energy, and a line perpendicular to LL′ the axis of minimum energy; and the excess of the time-integral of the energy of component velocity parallel to LL′ exceeds that of the component perpendicular to LL′ by 239·4, being $\sqrt{128{\cdot}8^2+201{\cdot}9^2}$. This is 7·25 per cent. of the total of $\Sigma\, l$ which is the time-integral of the total energy. Thus, in our result, we find a very notable deviation from the Boltzmann-Maxwell doctrine, which asserts for the present case that the time-integrals of the component kinetic energies are the same for all directions of the component. The percentage which we have found is not very large; and, most probably, summations for several successive 600 flights would present considerable differences, both of the amount of the deviation from equality and the direction of the axes of maximum and minimum energy. Still, I think there is a strong probability that the disproof of the Boltzmann-Maxwell doctrine is genuine, and the discrepance is somewhat approximately of the amount and direction indicated. I am supported in this view by scrutinizing the thirty sums for successive sets of twenty flights: thus I find $\Sigma l \cos 2\theta$ to be positive for eighteen out of thirty, and $\Sigma l \sin 2\theta$ to be negative for nineteen out of the thirty.

§ 38. A very interesting test-case is represented in the accompanying diagram, (fig. 6)—a circular boundary of semi-

Fig. 6.



circular corrugations. In this case it is obvious from the symmetry that the time-integral of kinetic energy of component motion parallel to any straight line must, in the long run, be equal to that parallel to any other. But the Boltzmann-Maxwell doctrine asserts, that the time-integrals of the kinetic energies of the two components, radial and transversal, according to polar coordinates, would be equal. To test this, I have taken the case of an infinite number of the semicircular corrugations, so that in the time-integral it is not necessary to include the times between successive impacts of the particle on any one of the semicircles. In this case the geometrical construction would, of course, fail to show the precise point Q at which the free path would cut the diameter AB of the semicircular hollow to which it is approaching; and I have evaded the difficulty in a manner thoroughly suitable for thermodynamic application such as the kinetic theory of gases. I arranged to draw lots for 1 out of the 199 points dividing AB into 200 equal parts. This was done by taking 100 cards*, 0, 1 . . . . . 98, 99, to represent distances from the middle point, and, by the toss of a coin, determining on which side of the middle point it was to be (plus or minus for head or tail, frequently changed to avoid possibility of error by bias). The draw for one of the hundred numbers (0 . . . . 99) was taken after very thorough shuffling of the cards in each case. The point of entry having been found, a large-scale geometrical construction was used to determine the successive points of impact and the inclination θ of the emergent path to the diameter AB. The inclination of the entering path to the diameter of the semicircular hollow struck at the end of the flight, has the same value θ. If we call the diameter of the large circle unity, the length of each flight is $\sin\theta$. Hence, if the velocity is unity and the mass of the particle 2, the time-integral of the whole kinetic energy is $\sin\theta$; and it is easy to prove that the time-integrals of the components of the velocity, along and perpendicular to the line from each point of the path to the centre of the large circle, are respectively $\theta\cos\theta$, and $\sin\theta-\theta\cos\theta$. The excess of the latter above the former is $\sin\theta-2\theta\cos\theta$. By summation for 143 flights we have found,

$$\Sigma\sin\theta=121{\cdot}3\ ;\ 2\Sigma\theta\cos\theta=108{\cdot}3\ ;$$

whence,

$$\Sigma\sin\theta-2\Sigma\theta\cos\theta=13{\cdot}0.$$

This is a notable deviation from the Boltzmann-Maxwell doctrine, which makes $\Sigma(\sin\theta-\theta\cos\theta)$ equal to $\Sigma\theta\cos\theta$. We have found the former to exceed the latter by a difference which amounts to 10·7 of the whole $\Sigma\sin\theta$.

Out of fourteen sets of ten flights, I find that the time-integral of the transverse component is less than half the whole in twelve sets, and greater in only two. This seems to prove beyond doubt that the deviation from the Boltzmann-Maxwell doctrine is genuine; and that the time-integral of the transverse component is certainly smaller than the time-integral of the radial component.

* I had tried numbered billets (small squares of paper) drawn from a bowl, but found this very unsatisfactory. The best mixing we could make in the bowl seemed to be quite insufficient to secure equal chances for all the billets. Full sized cards like ordinary playing-cards, well shuffled, seemed to give a very fairly equal chance to every card. Even with the full-sized cards, electric attraction sometimes intervenes and causes two of them to stick together. In using one's fingers to mix dry billets of card, or of paper, in a bowl, very considerable disturbance may be expected from electrification.

§ 39. It is interesting to remark that our present result is applicable (see § 38 above) to the motion of a particle, flying about in an enclosed space, of the same shape as the surface of a marlin-spike (fig. 7). Symmetry shows, that the axes of maximum or minimum kinetic energy must be in the direction of the middle line of the length of the figure and perpendicular to it. Our conclusion is that the time-integral of kinetic energy is maximum for the longitudinal component and minimum for the transverse. In the series of flights, corresponding to the 143 of fig. 6, which we have investigated, the number of flights is of course many times 143 in fig. 7, because of the reflections at the straight sides of the marlin-spike. It will be understood, of course, that we are considering merely motion in one plane through the axis of the marlin-spike.

§ 40. The most difficult and seriously troublesome statistical investigation in respect to the partition of energy which I have hitherto attempted, has been to find the proportions of translational and rotational energies in various cases, in each of which a rotator experiences multitudinous reflections at two fixed parallel planes between which it moves, or at one plane to which it is brought back by a constant force through its centre of inertia, or by a force varying directly as the distance from the plane. Two different rotators were considered, one of them consisting of two equal masses, fixed at the ends of a rigid massless rod, and each particle reflected on striking either of the planes ; the other consisting of two masses, 1 and 100, fixed at the ends of a rigid massless rod, the smaller mass passing freely across the plane without experiencing any force, while the greater is reflected every time it strikes. The second rotator may be described, in some respects more simply, as a hard massless ball having a mass = 1 fixed anywhere eccentrically within it, and another mass = 100 fixed at its centre. It may be called, for brevity, a biassed ball.

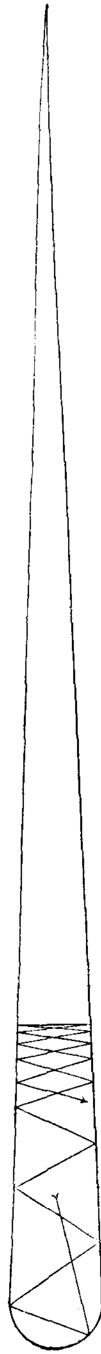


Fig. 7.

§ 41. In every case of a rotator whose rotation is changed by an impact, a transcendental problem of pure kinematics essentially occurs to find the time and configuration of the first impact; and another such problem to find if there is a second impact, and, if so, to determine it. Chattering collisions of one, two, three, four, five, or more impacts, are essentially liable to occur, even to the extreme case of an infinite number of impacts and a collision consisting virtually of a gradually varying finite pressure. Three is the greatest number of impacts we have found in any of our calculations. The first of these transcendental problems, occurring essentially in every case, consists in finding the smallest value of θ which satisfies the equation

$$\theta - i = \frac{\omega a}{v}(1 - \sin\theta);$$

where ω is the angular velocity of the rotator before collision; a is the length of a certain rotating arm; i its inclination to the reflecting plane at the instant when its centre of inertia crosses a plane F, parallel to the reflecting plane and distant a from it; and v is the velocity of the centre of inertia of the rotator. This equation is, in general, very easily solved by calculation (trial and error), but more quickly by an obvious kinematic method, the simplest form of which is a rolling circle carrying an arm of adjustable length. In our earliest work we performed the solution arithmetically, after that kinematically. If the distance between the two parallel planes is moderate in comparison with $2a$ (the effective diameter of the rotator), i for the beginning of the collision with one plane has to be calculated from the end of the preceding collision against the other plane by a transcendental equation, on the same principle as that which we have just been considering. But I have supposed the distance between the two planes to be very great, practically infinite, in comparison with $2a$, and we have therefore found i by lottery for each collision, using 180 cards corresponding to 180° of angle. In the case of the biassed globe, different equally probable values of i through a range of 360° was required, and we found them by drawing from the pack of 180 cards and tossing a coin for plus or minus.

§ 42. Summation for 110 flights of the rotator, consisting of two equal masses, gave as the time-integral of the whole energy, 200·03, and an excess of rotatory above translatory, 42·05. This is just 21 per cent. of the whole; a large deviation from the Boltzmann-Maxwell doctrine, which makes the time-integrals of translatory and rotatory energies equal.

§ 43. In the solution for the biassed ball (masses 1 and 100) we found great irregularities due to "runs of luck" in the toss for plus or minus, especially when there was a succession of five or six pluses or five or six minuses. We therefore, after calculating a sequence of 200 flights with angles each determined by lottery, calculated a second sequence of 200 flights with the equally probable set of angles given by the same numbers with altered signs. The summation for the whole 400 gave 555·55 as the time-integral of the whole energy, and an excess, 82·5, of the time-integral of the translatory, over the time-integral of the rotatory energy. This is nearly 15 per cent. We cannot, however, feel great confidence in this result, because the first set of 200 made the translatory energy less than the rotatory energy by a small percentage (2·3) of the whole, while the second 200 gave an excess of translatory over rotatory amounting to 35·9 per cent. of the whole.

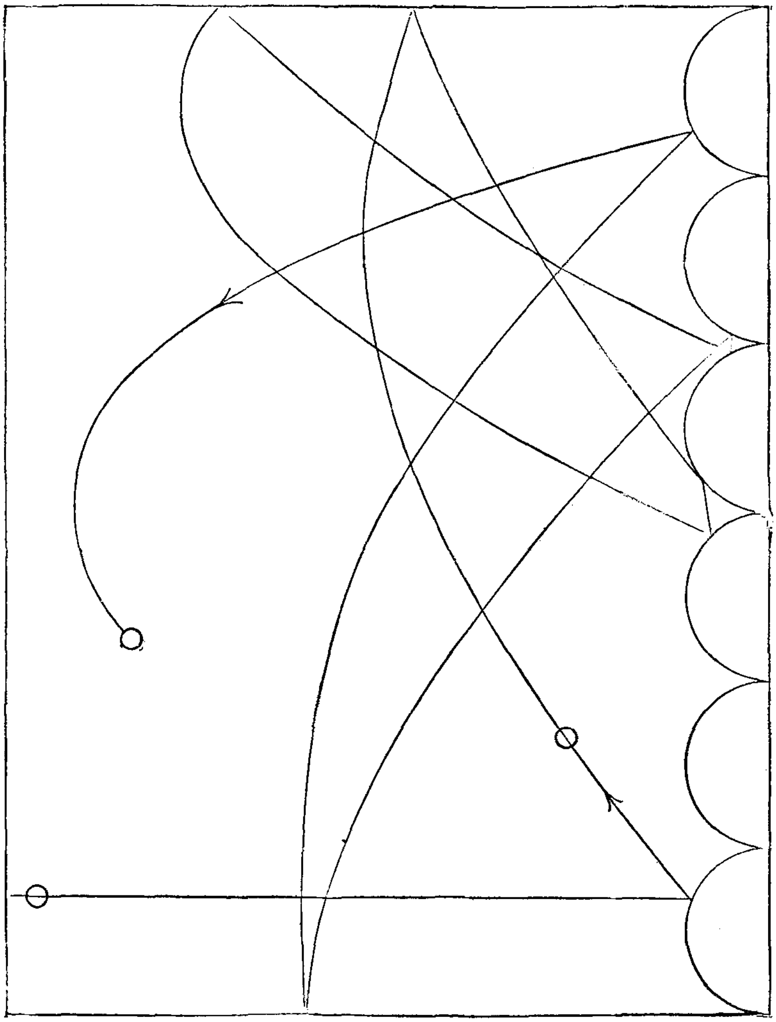
§ 44. All our examples considered in detail or worked out, hitherto, belong to Class I. of § 28. As a first example of Class II., consider a case merging into the geodetic line on a closed surface S. Instead of the point being constrained to remain on the surface, let it be under the influence of a field of force, such that it is attracted towards the surface with a finite force, if it is placed anywhere very near the surface on either side of it, so that if the particle be placed on S and projected perpendicularly to it, either inwards or outwards, it will be brought back before it goes farther from the surface than a distance h, small in comparison with the shortest radius of curvature of any part of the surface. The Boltzmann-Maxwell doctrine asserts that the time-integral of kinetic energy of component motion normal to the surface, would be equal to half the kinetic energy of component motion at right angles to the normal; by normal being meant a straight line drawn from the actual position of the point at any time perpendicular to the nearest part of the surface S. This, if true, would be a very remarkable proposition. If h is infinitely small, we have simply the mathematical condition of constraint to remain on the surface, and the path of the particle is exactly a geodetic line. If the force towards S is zero, when the distance on either side of S is $\pm h$, we have the case of a particle placed between two guiding surfaces with a very small distance, $2h$, between them. If S, and therefore each of the guiding surfaces, is in every normal section convex outwards, and if the particle is placed on the outer guide-surface, and projected in any direction in it, with any velocity, great or small, it will remain on that guide-surface for ever, and travel along a geodetic line. If now it be deflected very slightly from motion in that surface, so that it will strike against the inner guide-surface, we may be quite ready to learn, that the energy of knocking about between the two surfaces, will grow up from something very small in the beginning, till, in the long run, its time-integral is comparable with the time-integral of the energy of component motion parallel to the tangent plane of either surface. But will its ultimate value be exactly half that of the tangential energy, as the doctrine tells us it would be? We are, however, now back to Class I.; we should have kept to Class II., by making the normal force on the particle always finite, however great.

§ 45. Very interesting cases of Class II., § 28, occur to us readily in connexion with the cases of Class I. worked out in §§ 38, 41, 42, 43.

§ 46. Let the radius of the large circle in § 38 become infinitely great: we have now a plane F (floor) with *semicircular cylindric hollows*, or semicircular hollows as we shall say for brevity; the motion being confined to one plane perpendicular to F, and to the edges of the hollows. For definiteness we shall take for F the plane of the edges of the hollows. Instead now of a particle after collision flying along the chord of the circle of § 38, it would go on for ever in a straight line. To bring it back to the plane F, let it be acted on either (α) by a force towards the plane in simple proportion to the distance, or (β) by a constant force. This latter supposition (β) presents to us the very interesting case of an elastic ball bouncing from a corrugated floor, and describing gravitational parabolas in its successive flights, the durations of the different flights being in simple proportion to the component of velocity perpendicular to the plane F. The supposition (α) is purely ideal; but it is interesting because it gives a half curve of sines for each flight, and makes the times of flight from F after a collision and back again to F the same for all the flights, whatever be the inclination on leaving the floor and returning to it. The supposition (β) is illustrated in fig. 8, with only the variation that the corrugations are convex instead of concave, and that two vertical planes are fixed to reflect back the particle, instead of allowing it to travel indefinitely, either to right or to left.

§ 47. Let the rotator of §§ 41 to 43, instead of bouncing to and fro between two parallel planes, impinge only on one plane F, and let it be brought back by a force through its centre of inertia, either (α) varying in simple proportion to the distance of the centre of inertia from F, or (β) constant. Here, as in § 46, the times of flight in case (α) are all the same, and in (β) they are in simple proportion to the velocity of its centre of inertia when it leaves F or returns to it.

Fig. 8.



§ 48. In the cases of §§ 46, 47, we have to consider the time-integral for each flight of the kinetic energy of the component velocity of the particle perpendicular to F, and of the whole velocity of the centre of inertia of the rotator, which is itself perpendicular to F. If q denotes the velocity perpendicular to F of the particle, or of the centre of inertia of the rotator, at the instants of crossing F at the beginning and end of the flight, and if 2 denotes the mass of the particle or of the rotator so that the kinetic energy is the same as the square of the velocity, the time-integral is in case (α) $\frac{1}{2}q^2\mathrm{T}$ and in case (β) $\frac{1}{3}q^2\mathrm{T}$, the time of the flight being denoted in each case by T. In both (α) and (β), § 46, if we call 1 the velocity of the particle, which is always the same, we have $q^2=\sin^2\theta$, and the other component of the energy is $\cos^2\theta$. In § 47 it is convenient to call the total energy 1; and thus $1-q^2$ is the total rotational energy, which is constant throughout the flight. Hence, remembering that the times of flight are all the same in case (α) and are proportional to the value of q in case (β); in case (α), whether of § 46 or § 47, the time-integrals of the kinetic energies to be compared are as $\frac{1}{2}\Sigma q^2$ to $\Sigma(1-q^2)$, and in case (β) they are as $\frac{1}{3}\Sigma q^3$ and $\Sigma q(1-q^2)$.

Hence with the following notation—

In § 46 { Time-integral of kinetic energy perpendicular to F, $=\mathrm{V}$
  „ „ „ parallel to F, $=\mathrm{U}$

In § 47 { „ translatory energy $=\mathrm{V}$,
  „ rotatory „ $=\mathrm{R}$.

we have

$$\frac{\mathrm{V}-\mathrm{U}}{\mathrm{V}+\mathrm{U}}\begin{cases}=\dfrac{\Sigma(\frac{3}{2}q^2-1)}{\Sigma(1-\frac{1}{2}q^2)} & \text{in case } (\alpha),\\[2ex] =\dfrac{\Sigma(\frac{4}{3}q^3-q)}{\Sigma(q-\frac{2}{3}q^3)} & \quad\text{,,}\quad (\beta),\end{cases}$$

$$\frac{\mathrm{V}-\mathrm{R}}{\mathrm{V}+\mathrm{R}}\begin{cases}=\dfrac{\Sigma(\frac{3}{2}q^2-1)}{\Sigma(1-\frac{1}{2}q^2)} & \quad\text{,,}\quad (\alpha),\\[2ex] =\dfrac{\Sigma(\frac{4}{3}q^3-q)}{\Sigma(q-\frac{2}{3}q^3)} & \quad\text{,,}\quad (\beta).\end{cases}$$

§ 49. By the processes described above, q was calculated for the single particle and corrugated floor (§ 46), and for the rotator of two equal masses each impinging on a fixed plane (§§ 41, 42), and for the biassed ball (central and eccentric masses 100 and 1 respectively, §§ 41, 43). Taking these values of q, summing q, q^2, and q^3 for all the flights, and using the results in § 48, we find the following six results:

Single particle bounding from corrugated floor (semicircular hollows), 143 flights :—

$$\frac{V-U}{V+U}\begin{cases} = +\cdot 197 \text{ for isochronous sinusoidal flights.} \\ = +\cdot 136 \text{ for gravitational parabolic} \quad \text{,,} \end{cases}$$

Rotator of two equal masses, 110 flights :—

$$\frac{V-R}{V+R}\begin{cases} = -\cdot 179 \text{ for isochronous sinusoidal flights.} \\ = -\cdot 150 \text{ for gravitational parabolic} \quad \text{,,} \end{cases}$$

Biassed ball, 400 flights :—

$$\frac{V-R}{V+R}\begin{cases} = +\cdot 025 \text{ for isochronous sinusoidal flights.} \\ = -\cdot 014 \text{ for gravitational parabolic} \quad \text{,,} \end{cases}$$

The smallness of the deviation of the last two results from what the Boltzmann-Maxwell doctrine makes them, is very remarkable when we compare it with the 15 per cent. which we have found (§ 43 above) for the biassed ball bounding free from force, to and fro between two parallel planes.

§ 50. The last case of partition of energy which we have worked out statistically, relates to an impactual problem belonging partly to Class I., § 28, and partly to Class II. It was designed as a nearer approach to practical application in thermodynamics than any of those hitherto described. It is, in fact, a one-dimensional illustration of the kinetic theory of gases. Suppose a row of a vast number of atoms, of equal masses, to be allowed freedom to move only in a straight line between fixed bounding planes L and K. Let P the atom next K be caged between it and a parallel plane C, at a distance from it very small in comparison with the average of the free paths of the other particles ; and let Q, the atom next to P, be perfectly free to cross the cage-front C, without experiencing force from it. Thus, while Q gets freely into the cage to strike P, P cannot follow it out beyond the cage-front. The atoms being all equal, every simple impact would produce merely an interchange of velocities between the colliding atoms, and no new velocity could be introduced, if the atoms were perfectly hard (§ 16 above), because this implies that no three can be in collision at the same time. I do not, however, limit the present investigation to perfectly hard atoms. But, to simplify our calculations, we shall suppose P and Q to be infinitely hard. All the other atoms we shall suppose to have the property defined in § 21 above. They may pass through one another in a simple collision, and go asunder each with its previous velocity unaltered, if the differential velocity be sufficiently great ;

they must recoil from one another with interchanged velocities if the initial differential velocity was not great enough to cause them to go through one another. Fresh velocities will generally be introduced, by three atoms being in collision at the same time, so that even if the velocities were all equal to begin with, inequalities would supervene in virtue of three or more atoms being in collision at the same time; whether the initial differential velocities be small enough to result in two recoils, or whether one or both the mutual approaches lead to a passage or passages through one another. Whether the distribution of velocities, which must ultimately supervene, is or is not according to the Maxwellian law, we need not decide in our minds; but, as a first example, I have supposed the whole multitude to be given with velocities distributed among them according to that law (which, if they were infinitely hard, they would keep for ever after); and we shall further suppose equal average spacing in different parts of the row, so that we need not be troubled with the consideration of waves, as it were of sound, running to and fro along the row.

§ 51. For our present problem we require two lotteries, to find the influential conditions at each instant, when Q enters P's cage—lottery I. for the velocity (v) of Q at impact; lottery II. for the phase of P's motion. For lottery I. (after trying 837 small squares of paper with velocities written on them and mixed in a bowl, and finding the plan unsatisfactory), we took nine stiff cards, numbered 1, 2 . . . . 9, of the size of ordinary playing-cards, with rounded corners, with one hundred numbers written on each in ten lines of ten numbers. The velocities on each card are shown in the following table. The number of times each velocity occurs was chosen to fulfil as nearly as may be the Maxwellian law, which is $Cdv\epsilon^{-\frac{v^2}{k}}$ = the number of velocities between $v+\frac{1}{2}dv$ and $v-\frac{1}{2}dv$. We took $k=1$, which, if dv were infinitely small, would make the mean of the squares of the velocities equal exactly to $\cdot 5$; we took $dv=\cdot 1$ and $Cdv=108$, to give, as nearly as circumstances would allow, the Maxwellian law, and to make the total number of different velocities 900. The sum of the squares of all these 900 velocities is 468·4, which divided by 900 is ·52. In the practice of this lottery, the numbered cards were well shuffled and then one was drawn; the particular one of the hundred velocities on this card to be chosen was found by drawing one card from a pack of one hundred numbered 1, 2 . . . 99, 100. In lottery II. a pack of one hundred cards is used to draw one of one hundred decimal numbers from ·01 to 1·00. The decimal drawn, called α, shows the proportion of the whole period of P from the cage-front C, to K, and back to C, still unperformed at the instant when Q crosses C. Now remark, that

TABLE SHOWING THE NUMBER OF THE DIFFERENT VELOCITIES ON THE DIFFERENT CARDS.

Velocity.	·1	·2	·3	·4	·5	·6	·7	·8	·9	1·0	1·1	1·2	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1	2·2	
Card 1	100																						
„ 2	7	93																					
„ 3		10	90																				
„ 4			9	91																			
„ 5				1	84	15																	
„ 6						60	40																
„ 7							26	57	17														
„ 8									31	40	29												
„ 9											3	26	19	15	11	9	6	4	3	2	1	1	Σv
Sums of velocities	107	103	99	92	84	75	66	57	48	40	32	26	19	15	11	9	6	4	3	2	1	1	900

if Q overtakes P in the first half of its period, it gives its velocity, v, to P and follows it inwards ; and therefore there must be a second impact when P meets it after reflexion from K and gives it back the velocity v which it had on entering. If Q meets P in the second half of its period, Q will, by the first impact, get P's original velocity, and may with this velocity escape from the cage. But it may be overtaken by P before it gets out of the cage, in which case it will go away from the cage with its own original velocity v unchanged. This occurs always if, and never unless, u is less than $v\alpha$; P's velocity being denoted by u, and Q's by v. This case of Q overtaken by P can only occur if the entering velocity of Q is greater than the speed of P before collision. Except in this case, P's speed is unchanged by the collision. Hence we see, that it is only when P's speed is greater than Q's before collision, that there can be interchange, and this interchange leaves P with less speed than Q. If every collision involved interchange, the average velocity of P would be equalized by the collisions to the average velocity of Q, and the average distribution of different velocities would be identical for Q and P. Non-fulfilment of this equalizing interchange can, as we have seen, only occur when

Q's speed is less than P's, and therefore the average speed and the average kinetic energy of P must be less than the average kinetic energy of Q.

§ 52. We might be satisfied with this, as directly negativing the Boltzmann-Maxwell doctrine for this case. It is, however, interesting to know, not only that the average kinetic energy of Q is greater than that of the caged atom, but, further, to know how much greater it is. We have therefore worked out summations for 300 collisions between P and Q, beginning with $u^2 = \cdot 5$ ($u = \cdot 71$), being approximately the mean of v^2 as given by the lottery. It would have made no appreciable difference in the result if we had begun with any value of u, large or small, other than zero. Thus, for example, if we had taken 100 as the first value of u, this speed would have been taken by Q at the first impact, and sent away along the practically infinite row, never to be heard of again; and the next value of u would have been the first value drawn by lottery for v. Immediately before each of the subsequent impacts, the velocity of P is that which it had from Q by the preceding impact. In our work, the speeds which P actually had at the first sixteen times of Q's entering the cage were ·71, ·5, ·3, ·2, ·2, ·1, ·1, ·2, ·2, ·5, ·7, ·2, ·3, ·6, 1·5, ·5—from which we see how little effect the choice of ·71 for the first speed of P had on those that follow. The summations were taken in successive groups of ten; in every one of these Σv^2 exceeded Σu^2. For the 300 we found $\Sigma v^2 = 148 \cdot 53$ and $\Sigma u^2 = 61 \cdot 62$, of which the former is 2·41 times the latter. The two ought to be equal according to the Boltzmann-Maxwell doctrine. Dividing Σv^2 by 300 we find ·495, which chances to more nearly the ·5 we intended than the ·52 which is on the cards (§ 51 above). A still greater deviation (2·71 instead of 2·41) was found by taking Σv^3 and $\Sigma u'^2 v$ to allow for greater probability of impact with greater than with smaller values of v; u' being the velocity of P after collision with Q.

§ 53. We have seen in § 51 that Σu^2 must be less than Σv^2, but it seemed interesting to find how much less it would be with some other than the Maxwellian law of distribution of velocities. We therefore arranged cards for a lottery, with an arbitrarily chosen distribution, quite different from the Maxwellian. Eleven cards, each with one of the eleven numbers 1, 3 . . . . 19, 21, to correspond to the different velocities ·1, ·3 . . . . 1·9, 2·1, were prepared and used instead of the nine cards in the process described in § 51 above. In all except one of the eleven tens, Σv^2 was greater than Σu^2, and for the whole 110 impacts we found $\Sigma v^2 = 179 \cdot 90$, and $\Sigma u^2 = 97 \cdot 66$; the former of these is 1·84 times the latter. In this case we found the ratio of Σv^3 to $\Sigma u'^2 v$ to be 1·87.

§ 54. In conclusion, I wish to refer, in connexion with Class II., § 28, to a very interesting and important application of the doctrine, made by Maxwell himself, to the equilibrium of a tall column of gas under the influence of gravity. Take, first, our one-dimensional gas of § 50, consisting of a straight row of a vast number of equal and similar atoms. Let now the line of the row be vertical, and let the atoms be under the influence of terrestrial gravity, and suppose, first, the atoms to resist mutual approach, sufficiently to prevent any one from passing through another with the greatest relative velocity of approach that the total energy given to the assemblage can allow. The Boltzmann-Maxwell doctrine (§ 18 above), asserting as it does that the time-integral of the kinetic energy is the same for all the atoms, makes the time-average of the kinetic energy the same for the highest as for the lowest in the row. This, if true, would be an exceedingly interesting theorem. But now, suppose two approaching atoms not to repel one another with infinite force at any distance between their centres, and suppose energy to be given to the multitude sufficient to cause frequent instances of two atoms passing through one another. Still the doctrine can assert nothing but that the time-integral of the kinetic energy of any one atom is equal to that of any other atom, which is now a self-evident proposition, because the atoms are of equal masses, and each one of them in turn will be in every position of the column, high or low. (If in the row there are atoms of different masses, the Waterston-Maxwell doctrine of equal average energies would, of course, be important and interesting.)

§ 55. But now, instead of our ideal one-dimensional gas, consider a real homogeneous gas, in an infinitely hard vertical tube, with an infinitely hard floor and roof, so that the gas is under no influence from without, except gravity. First, let there be only two or three atoms, each given with sufficient velocity to fly against gravity from floor to roof. They will strike one another occasionally, and they will strike the sides and floor and roof of the tube much more frequently than one another. The time-averages of their kinetic energies will be equal. So will they be if there are twenty atoms, or a thousand atoms, or a million, million, million, million, million atoms. *Now* each atom will strike another atom much more frequently than the sides or floor or roof of the tube. In the long run each atom will be in every part of the tube as often as is every other atom. The time-integral of the kinetic energy of any one atom will be equal to the time-integral of the kinetic energy of any other atom. This truism is simply and solely all that the Boltzmann-Maxwell doctrine asserts for a vertical column of a homogeneous monatomic gas. It is, I believe, a general impression that the Boltzmann-Maxwell doctrine, asserting a law of partition of the kinetic part of the whole energy, includes obviously a theorem that the average kinetic energy of the atoms in the upper parts of a vertical column of gas, is equal to that of the atoms in the lower parts of the column. Indeed, with the wording of Maxwell's statement, § 18, before us, we might suppose it to assert that two parts of our vertical column of gas, if they contain the same number of atoms, must have the same kinetic energy, though they be situated, one of them near the bottom of the column, and the other near the top. Maxwell himself, in his 1866 paper ("The Dynamical Theory of Gases") *, gave an independent synthetical demonstration of this proposition, and did not subsequently, so far as I know, regard it as immediately deducible from the partitional doctrine generalized by Boltzmann and himself several years after the date of that paper.

§ 56. Both Boltzmann and Maxwell recognized the experimental contradiction of their doctrine presented by the kinetic theory of gases, and felt that an explanation of this incompatibility was imperatively called for. For instance, Maxwell, in a lecture on the dynamical evidence of the molecular constitution of bodies, given to the Chemical Society, Feb. 18, 1875, said: "I have put before you what "I consider to be the greatest difficulty yet encountered by "the molecular theory. Boltzmann has suggested that we "are to look for the explanation in the mutual action between "the molecules and the ethereal medium which surrounds "them. I am afraid, however, that if we call in the help of "this medium we shall only increase the calculated specific "heat, which is already too great." Rayleigh, who has for the last twenty years been an unwavering supporter of the Boltzmann-Maxwell doctrine, concludes a paper "On the Law of Partition of Energy," published a year ago in the Phil. Mag., Jan. 1900, with the following words: "The difficulties "connected with the application of the law of equal partition "of energy to actual gases have long been felt. In the case of "argon and helium and mercury vapour, the ratio of specific "heats (1·67) limits the degrees of freedoms of each molecule

* Addition, of date December 17, 1866. Collected works, vol. ii. p. 76.

"to the three required for translatory motion. The value "(1·4) applicable to the principal diatomic gases, gives room "for the three kinds of translation and for two kinds of "rotation. Nothing is left for rotation round the line joining "the atoms, nor for relative motion of the atoms in this line. 'Even if we regard the atoms as mere points, whose rotation "means nothing, there must still exist energy of the last-"mentioned kind, and its amount (according to law) should "not be inferior.

"We are here brought face to face with a fundamental "difficulty, relating not to the theory of gases merely, but "rather to general dynamics. In most questions of dynamics, "a condition whose violation involves a large amount of "potential energy may be treated as a constraint. It is on "this principle that solids are regarded as rigid, strings as "inextensible, and so on. And it is upon the recognition "of such constraints that Lagrange's method is founded. "But the law of equal partition disregards potential energy. "However great may be the energy required to alter the "distance of the two atoms in a diatomic molecule, practical "rigidity is never secured, and the kinetic energy of the "relative motion in the line of junction is the same as if the "tie were of the feeblest. The two atoms, however related, "remain two atoms, and the degrees of freedom remain six "in number.

"What would appear to be wanted is some escape from "the destructive simplicity of the general conclusion."

The simplest way of arriving at this desired result is to deny the conclusion; and so, in the beginning of the twentieth century, to lose sight of a cloud which has obscured the brilliance of the molecular theory of heat and light during the last quarter of the nineteenth century.

II. *The Absorption of the Ionized* Phosphorus Emanation in Tubes.*—II. *By* C. Barus†.

1. FOR reasons of both theoretical and practical import it is next necessary to ascertain the precise conditions under which the phosphorus nucleus vanishes on passing

* Whoever writes on subjects relating, like the present, to certain features of ionization is obliged to make free use of the admirable work (Thomson, C. T. R. Wilson, Townsend, Rutherford, Zeleny, and others), which has been sent out by the Cavendish Laboratory under the direction of Prof. J. J. Thomson. These researches, like those of Chattock, Elster and Geitel, and others (*cf.* H. Becquerel in 'Nature,' Feb. 21st, p. 396, 1901), are so recent and well known that detailed reference would be cumbersome; but I desire to make my acknowledgments here.

† Communicated by the Author.