Maxwell's contribution to the development of molecular physics and statistical methods

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Maxwell's fundamental studies in the period 1859–1879 on molecular physics and allied subjects are considered. His two very important papers of 1859 and 1866 on the dynamical theory of gases are analyzed, as are his two last extensive papers of 1879 on transport phenomena in rarefied gases and on statistical mechanics. Other papers, notes, lectures, and his book on the theory of heat are also considered. Particular attention is devoted to Maxwell's pioneering contribution to the development of statistical methods and his deep understanding of the statistical origin of the second law of thermodynamics. The connection between the work of Maxwell and that of Clausius and Boltzmann is discussed. It is emphasized that the development by Boltzmann of statistical methods was based to a large degree on the pioneering work of Maxwell. The influence of Maxwell's ideas on the development of the theory of inhomogeneous gases in the present century is also demonstrated.

CONTENTS

1. INTRODUCTION

Besides his investigations into electromagnetism, an important part of Maxwell's scientific work was his investigations into molecular physics, which he began in 1859 with a study of problems in the kinetic theory of gases. In his first and fundamental study of these questions, "Illustrations of the dynamical theory of gases,"[1] Maxwell applied the methods of probability theory to the disordered motions of colliding gas molecules, regarded as perfectly elastic spheres. He found for such spheres the equilibrium distribution function of their velocities—the famous Maxwell distribution, which laid the foundation for the development of the methods of statistical physics. On the basis of this model of a gas, Maxwell provided for the first time, using the concept of the mean free path introduced earlier by Clausius, an elementary theory of transport processes, namely, internal friction, diffusion, and heat conduction in gases. This theory stimulated further experimental and theoretical study of these irreversible processes.

In the following years, Maxwell made a number of investigations in molecular physics and continued to develop statistical methods. Of great importance was his major paper "On the dynamical theory of gases,"[2] in 1866, in which he gave a new derivation of the velocity distribution function of molecules based on a consideration of direct and inverse collisions of the molecules. In this paper, Maxwell developed transport theory in a very general form without using the concept of the mean free path, and he then applied the theory to the processes of diffusion, internal friction, and heat conduction.

He also considered a gas in the field of a gravity force, which subsequently led him to the solution to the problem of the energy distribution function of molecules in an arbitrary force field. In a short paper in 1873, "On a final state of a system of molecules in motion subject to forces of any kind,"[3] Maxwell gave a simple derivation of this function (the Maxwell–Boltzmann distribution function, including the Boltzmann factor). In the same year he published the paper "On Loschmidt's experiments on diffusion in relation to the kinetic theory of gases,"[4] in which he calculated the diameters of molecules for a number of gases from the data of experiments on diffusion. In 1879—the last year of his life—he published two large fundamental papers: "On stresses in rarefied gases arising from inequalities of temperature,"[5] and "On Boltzmann's theorem on the average distribution of energy in a system of material points."[6] In the first of these papers, general transport theory was applied to rarefied gases. The second paper was also very important. In it, statistical methods were generalized and applied to arbitrary systems of interacting particles and not only to gases, which prepared the way for the investigations of Gibbs in statistical mechanics.

In the above fundamental studies and in a number of papers and notes, Maxwell examined many problems of molecular physics. His textbook Theory of Heat[7] was published in 1871; the major part of it is devoted to a phenomenological study of thermal phenomena. Five editions of this textbook were published during his life. Considerable attention is paid to thermodynamics,

and in the final chapter, which is of particular interest, a "Maxwell demon" appears for the first time in the section on the limits of applicability of the second law of thermodynamics. Maxwell's slender volume Matter and Motion[8] (1873) contains an exposition of his physical and philosophical views on the nature of molecular motion.

Maxwell successfully combined fundamental studies of basic questions of molecular physics with active popularization of atomic and molecular teaching. In a number of papers (in particular, in the Encyclopedia Britannica, in public appearances and lectures, in book reviews, and in brief notes in Nature, Maxwell explained his views on the nature and properties of atoms and molecules and justified the introduction of statistical methods for studying molecular systems.

More than 30 papers by Maxwell, both the pure research papers as well as those of a pedagogical and popular nature, are devoted either fully or in part to problems of molecular physics and allied questions. It is very important to consider Maxwell's papers as a whole and taking into account the development of his ideas over the period of 20 years during which he worked on these questions (1859–1879). Unfortunately, it is often the case that only individual papers of his, generally the first,[1] are considered (and then only in part); this does not enable one to form a sufficiently complete judgement about the fundamental contribution of Maxwell to molecular physics and the part he played in the development of statistical methods.

The aim of the present paper is to acquaint the reader with the contents of Maxwell's original papers and on the basis of a systematic analysis of them give a true estimate of the contribution made by Maxwell to molecular physics and statistical mechanics.

Most of the papers we consider appeared in the two-volume edition of his scientific papers,[9] which included his papers Refs. 1–6, some other papers on molecular physics and allied questions, and papers and lectures of a general nature important for understanding his views. We have also used papers and notes published by Maxwell in periodicals of that time not included in Ref. 9 and, in addition, some papers that were not published by him during his life and appeared only fully or in part after his death. Only the paper Ref. 1 and some popular papers and lectures have been translated into Russian; these are contained mainly in the collection of Ref. 10.

In the analysis of Maxwell's papers, it is important to know details of his life and work. The first and fullest biography of Maxwell was written by Campbell and Garnett[11]; among the later studies, we should mention the bibliographical papers of Everitt[12] (who gives a large section on Maxwell's studies in statistical and molecular physics; his paper gives numerous references to the literature on Maxwell), Jones,[13] and the detailed biography of Maxwell written by Kartsev[14] (who has also written the interesting paper Ref. 15).

Maxwell's letters, including those published in Ref. 11 and his letters to Stokes[16] and to Tait,[17] also contain important material.

Among the historicoscientific investigations devoted to the papers of Maxwell in which we are interested, we should mention those of Brush[18,19] (the second in collaboration with Everitt) and particularly Ref. 20, and also the papers of Garber.[21-23] In the book The Kind of Motion We Call Heat,[24] which contains much well-arranged material, Brush considers Maxwell's papers on the kinetic theory of gases and allied subjects from the point of view of the development of this theory in the 19th century (see also Brush's book on kinetic theory[25]). In their papers Refs. 26 and 27, Klein and Heimann analyze some ideas advanced by Maxwell.

Individual papers of Maxwell have been considered in Soviet and non-Soviet courses on the history of physics,[28-33] and also in Gel'fer's book[34] on the history of thermodynamics and statistical physics.

Some papers about Maxwell and the significance of his studies are included in the book of Ref. 10, which contains a useful bibliography.

2. SOURCES OF MAXWELL'S INVESTIGATIONS ON THE MOLECULAR-KINETIC THEORY OF GASES

Already at an early stage in the development of the study of heat two directions appeared. The first was based on a theory of heat as a particular substance—caloric, or thermogen; the second, the molecular-kinetic direction, was based on the idea of heat as a kind of motion of particles of a body.

At the very beginning of his first paper on the molecular-kinetic theory of gases,[1] Maxwell wrote: "So many of the properties of matter, especially when in the gaseous form, can be deduced from the hypothesis that their minute parts are in rapid motion, the velocity increasing with the temperature, that the precise nature of this motion becomes a subject of rational curiosity," (Ref. 1, p.19 in Phil. Mag.).

Maxwell then referred to the investigations of "Daniel Bernoulli, Herapath, Joule, Krönig, Clausius, etc."[1]

As is well known, the basic ideas of the molecular-kinetic theory of gases were formulated as early as 1738 by the Swiss scientist Daniel Bernoulli in the tenth chapter, entitled "On the properties and motions of elastic fluid media, in particular air," of his book on hydrodynamics.[35] According to Bernoulli, elastic fluid bodies—gases—consist of an infinitely large number of very small particles moving "extremely rapidly in different directions and possessing gravity" (Ref. 35, p. 282). Heat is associated with the motion of these particles, "since it is known that when the internal motion of particles increases everywhere the heat increases" (Ref. 35, p. 285). Bernoulli formulates the theorem that "in every air of any density but possessing the same degree of heat the elasticities are proportional to

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[1] Maxwell did not know about Lomonosov's work; the papers of Waterston were published after Maxwell's death (see the book Ref. 24 for a discussion of Waterston's papers).

the densities, and therefore the increments of the elasticity due to equal increases in heat are proportional to the densities" (Ref. 35, p. 286).

In the first half of the 19th century, the ideas of the kinetic theory of gases were developed by the English physicist Herapath.[36,37] In 1847, he explained his ideas in Mathematical Physics[28] (Maxwell subsequently referred to this book in Refs. 2 and 39). Herapath explained the laws of ideal gases, diffusion phenomena, and the propagation of sound in gases on the basis of the hypothesis of motion and collisions of particles of gas regarded as elastic spheres. The gas particles are displaced constantly with high velocity along sections of straight lines. A consequence of this type of motion is the pressure which a gas exerts on any surface placed in the path of the particles. However, Herapath obtained an incorrect result: the gas pressure is not proportional to the absolute temperature but to its square (see the book Ref. 24 for more details of Herapath's work).

In 1848, Joule, who had been occupied with questions of the theory of heat, gave a lecture to the Manchester Literary and Philosophical Society that became his best known work: "Some remarks on heat and the constitution of elastic fluids."[40] Joule bases his calculations on Herapath's model, which appears to him "somewhat simpler" than the hypothesis of heat as a rotational motion of particles, although the latter "accords equally well with the phenomena" (Ref. 40, p. 36 in Philos. Mag.). By means of this model, Joule calculated for the first time the velocity of hydrogen molecules.

To calculate the velocity of hydrogen particles, Joule considers "an envelope of the size and shape of a cubic foot to be filled with hydrogen gas," which at normal atmospheric and room temperature has a definite weight. Assuming "the above quantity to be divided into three equal and indefinitely small particles," each having 1/3 of the total weight of the particles, "and further, that each of these particles vibrates between opposite sides of the cube, and maintains a uniform velocity except at the instant of impact," Joule finds the velocity with which each such particle must move in order to compensate the atmospheric pressure on each side of the cube. The obtained velocity will be able "to produce the atmospheric pressure, whether the particles strike each other before they arrive at the sides of the cubical vessel, whether they strike the sides obliquely, ..." Assuming further that the particles of hydrogen do not have an appreciable size, Joule obtains for the hydrogen molecules a velocity equal to 6225 feet per second (1897 m/sec).

In 1856, the German physicist Krönig, who at that time was fairly well known in Germany, published a short (eight pages) paper entitled "Grundzüge einer Theorie der Gase."[41] According to Krönig's hypothesis, gases consist of atoms which behave as rigid, perfectly elastic spheres moving with a definite velocity within an empty space. They interact with each other only in collisions. Krönig considers a gas in a vessel having the shape of a parallelepiped, and assumes that the atoms move parallel to the edges of the vessel along the directions $+x, -x, +y, -y, +z, -z$, one sixth of the total number of atoms moving in each direction. The velocity c of all the atoms is assumed to be the same. Comparing the obtained expression for the pressure (proportional to mc^2, where m is the mass of an atom) with Clapeyron's equation, Krönig concludes that "the vis viva of an atom is nothing else but the temperature measured from the absolute zero" (Ref. 41, p. 318).

In 1873, Maxwell wrote: "The further development of the theory is generally supposed to have begun with a paper by Krönig, which does not, however, so far as I can see, contain any improvement on what had gone before. It seems, however, to have drawn the attention of Professor Clausius to the subject, and to him we owe a very large part of what has been since accomplished," (Ref. 39, p.75). It should be noted that during this period (up to 1873) Maxwell himself had already made a very appreciable contribution to the kinetic theory of gases in his Refs. 1 and 2 (see the following section).

In 1857, Clausius published the very important paper "Über die Art der Bewegung, welche wir Wärme nennen."[42] This paper of Clausius laid the foundation of the modern development of the kinetic theory of gases.[2] Clausius, like Krönig, whose paper he quotes, considers the translational motion of gas particles, but, in contrast to Krönig, he speaks of molecules, and not atoms. He also points out the possibility of rotational and vibrational motion of molecules, which will influence the "total heat contained in a gas" and will be "particularly important for gases of complicated chemical composition, for which there are many atoms in a molecule" (Ref. 42, p. 355). Clausius assumes that by virtue of the large number of collisions a definite distribution of the energies is established on the average for the molecules between the translational and rotational motion and that "with regard to the translational motion the molecules satisfy the ordinary laws of elasticity." Clausius explains the pressure of its gas and its dependence on the volume and temperature "as was done by Krönig" by considering elastic collisions with a wall of a large number of molecules in translational motion. In the mathematical appendix to the paper, Clausius makes the corresponding calculation without assuming that one third of the molecules moves at right angles to the wall. He takes into account the equal probability of the directions of motion of the molecules. He assumes that the momentum transferred to the wall is $2mu \cos\vartheta$, where m is the mass of a molecule, u is its velocity, and ϑ is the angle between the direction of the velocity of the molecule and the normal to the wall, and he integrates over the angles. Clausius assumes that the velocity of all the molecules is the same and equal to some mean velocity. In this connection, he writes: "... in reality, of course, there is a very great variety in the velocities of the individual molecules. However, in calculations one can ascribe a certain mean velocity to all the molecules. As is clear from the following formulas, to obtain the same pressure

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[2] Brush took the title of this paper as the title of his book[24] on the history of the kinetic theory of gases in the 19th century.

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this mean velocity must be chosen such that the *vis viva* of all the molecules at the mean velocity is the same as at the actually occurring velocities" (Ref. 42, p. 372). It was only Maxwell who was subsequently able to find the law of the distribution of the molecules with respect to the velocities (see below). Clausius calculated the velocity of the molecules of oxygen, nitrogen, and hydrogen at the freezing point of water and obtained the values 461 m/sec, 422 m/sec, and 1844 m/sec, respectively (Ref. 42, p. 370).

Clausius considers the conditions of strict validity of the "law of Mariotte and the law of Gay-Lussac and the laws associated with them." Three conditions must be satisfied: the actual volume of the molecules must be small compared with the total volume of the gas, the time of a collision must be short compared with the time between two collisions, and the influence of the molecular forces must be negligibly small. Otherwise, "there are various deviations from the simple gas laws, and these are the larger, the less the molecular state of the gas corresponds to these conditions" (Ref. 42, p. 358).

Clausius also considers the question of how, from the point of view of the molecular-kinetic theory, the solid state differs from the liquid, and he discusses the question of the evaporation and density of saturated vapors together with other questions.

Clausius's paper stimulated a number of objections. In particular, Bays-Ballot[43] pointed out that the high velocity of the molecules does not correspond to observed phenomena, namely, the slow diffusion of gases, the slow movement of smoke, and the existence of an edge of the atmosphere. Continuing to develop his theory, Clausius dealt with these objections in his following paper, which was devoted to the mean free path of gas molecules.[44]

To calculate the mean free path, Clausius introduced into the theory the concept of the sphere of influence of molecules. He points out that in the absence of chemical affinity it is necessary to distinguish two kinds of molecular forces, "namely, when two molecules approach, a force of attraction begins to act, this becoming appreciable at a certain distance and increasing with decreasing distance, but when the molecules are in the immediate proximity of each other a force arises which tends to separate them" (Ref. 44, p. 241). As a result, in the case of impact distances (using the modern terminology) greater than some mean distance ρ, there will be only a curving of the paths of the molecules, whereas at impact parameters less than ρ the molecules will rebound from each other. This latter case Clausius regards as a *collision*, and he defines the *sphere of influence* of a molecule as a sphere of radius ρ described around the center of gravity of the molecule. He then finds the mean free path, "the mean length of the path between two such collisions," which he expresses in terms of ρ and the length λ, which is equal to the distance between the nearest molecules when they are uniformly distributed in the volume of the gas. Under the assumption that only one molecule moves, with a certain mean velocity v, and that the re-

maining molecules are fixed, Clausius obtains for the mean free path the formula $l' = \lambda^3/\pi\rho^2$. When allowance is made for the mean relative velocity of the molecules, which, according to Clausius, is $4v/3$, the mean free path is $l = 3l'/4 = 3\lambda^3/4\pi\rho^2$. Considering the ratio of the volume of the gas λ^3 per molecule to the volume $(4/3)\pi\rho^3$ of a sphere of radius ρ, Clausius assumes that this ratio is equal to 1000,[3] whence $\lambda/\rho = 16.12$, $l = 1000\rho = 61\lambda$ (Ref. 44, pp. 249–250). Accordingly, we find that the mean free path exceeds the length λ by not more than two orders of magnitude, i.e., it is a distance much less than observable distances.

It is important to emphasize that in deriving his formula for the mean free path of molecules Clausius used arguments from the theory of probability.

At the beginning of the 19th century, when Laplace's famous paper was published,[45] probability was regarded as either a purely philosophical or a purely mathematical subject. In 1843, Mill discussed the logic of the theory of probability in his book A System of Logic.[46] However, the methods of probability theory were applied mainly to the description of social phenomena. In 1849, Adolph Quetelet[47] published a book on the use of probability methods in politics and the theory of games.

On the basis of Laplace's paper a theory of errors was created, and this laid the foundations for the use of probability methods in physics. In 1849, Clausius used probability ideas in his paper "Über die Natur derjenigen Bestand theile der Erdatmosphäre, durch welche Lichtreflexion an derselban bewirkt wird."[48] However, examples of the use of probability methods were few and unrelated.

Probability arguments were invoked by Krönig in his paper of Ref. 41 discussed above. In analyzing the motion of gas particles, Krönig used the idea of the randomness of this motion. He wrote: "for the atoms of a gas, a smooth wall must be regarded as very uneven, and therefore the trajectory of each atom must be so disordered as to preclude any calculation. However, in accordance with the laws of the theory of probabilities, complete order can be assumed in place of this complete disorder" (Ref. 41, p. 318).

Already in 1857 Clausius used probability ideas in Ref. 42: Whatever the individual motions of the atoms and molecules, the final results will contain statistical mean values. Although the individual collisions of the molecules can take place in accordance with any law, "in the investigation of the combined influence of a large number of molecules, it is possible to ignore the irregularities of the individual collisions and assume that with regard to the translational motion the molecules follow the general laws of elasticity" (Ref. 42, p. 356).

It should be noted that in introducing probability ideas into kinetic theory Clausius regarded them only as obvious and more convenient mathematical devices that strongly simplify the calculations. It is therefore evi-

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[3] That is, equal in order of magnitude to the ratio of the density of the liquid to the density of the gas.

dent why, in giving the final expression for the mean free path, Clausius did not regard it as necessary to give a derivation based on probability arguments of the coefficient 3/4, but simply included this value of the coefficient in the final result. In his early papers, Clausius did not see important differences between microscopic and macroscopic processes, all the phenomena of nature satisfying for him mechanical laws. Therefore, "in deriving general expressions, we do not need to take into account at all random differences. It is only in numerical calculations that we must remember that the mean value can change" (Ref. 34, p. 366).

Clausius was the immediate predecessor of Maxwell in developing the kinetic theory of gases. Clausius's investigations had a great influence of forming Maxwell's interest in this theory. It was after he became acquainted with the English translation of Clausius's paper, published in February 1859 in the Philosophical Magazine,[44] that Maxwell, as he recognized in Ref. 2, occupied himself with the kinetic theory of gases.[4]

Maxwell wrote of Clausius: "After reading his investigation (Philos. Mag. Feb. 1859) of the distance described by each molecule between successive collisions, I published some propositions ("Illustrations of the Dynamical Theory of Gases," Philos. Mag. 1860, January and July) on the motions and collisions of perfectly elastic spheres, and deduced several properties of gases, ..." (Ref. 2, p. 29).

It is interesting to note that, as can be seen from Maxwell's letter to Stokes on May 31, 1859 (Ref. 16, p. 8–10), he originally intended to refute Clausius's theory, regarding its consequences as contradicting experience. However, already in Ref. 1 Maxwell adopted Clausius's ideas, in particular the mean free path. Subsequently, Maxwell regarded highly Clausius's contribution to the development of the molecular-kinetic theory. In Ref. 2, he emphasized: "It is to Professor Clausius, of Zurich, that we owe the most complete dynamical theory of gases."

In a letter of 1871, found in the papers of Thomson (Lord Kelvin), Maxwell wrote about Clausius's contribution as follows:

"10. The great development of the theory is due to Clausius.

α. The arrangement of the molecules at any instant is perfectly general.

β. The impacts of the molecules against each other are taken fully into account.

γ. The relation between their diameter, the number in a given space and the mean length of path is determined.

δ. Mathematical methods are introduced for dealing *statistically* with immense numbers of molecules by ar-

ranging them in groups according to their directions, velocities, etc.

ε. The slowness of diffusion is accounted for, and steps taken towards a complete theory.

ξ. Theory of evaporation and maximum density of vapours.

η. Theory of the change of partners among the molecules of compound bodies and the theory of electrolytic conduction under the smallest electromotive force, etc., etc.

θ. Internal energy of molecules." (Ref. 49, p. 211).

3. GENERAL REVIEW OF MAXWELL'S INVESTIGATIONS OF MOLECULAR PHYSICS AND ALLIED SUBJECTS

The first and best known of Maxwell's papers on the molecular-kinetic theory of gases[1] (which at that time he called a dynamical theory[5]) was presented by him on September 21, 1859 at the annual meeting of the British Association for the Advancement of Science, which was held at Aberdeen, where Maxwell at that time held a chair at the University.

In his paper, a central position is occupied by a study of transport phenomena using the ideas about the mean free path introduced earlier by Clausius.[44] Maxwell writes that these phenomena "... seem to indicate the possibility of determining accurately the mean length of path which a particle describes between two successive collisions." Maxwell bases his treatment on a model in which a gas consists of moving "small, hard, and perfectly elastic spheres acting on one another only during impact."

Maxwell refers to a different model of a gas which leads "to the same results." According to this model the particles of the gas are "centres of force, of which the action is insensible except at a certain small distance, when it suddenly appears as a repulsive force of very great intensity." Maxwell subsequently used such a model in 1866 in Ref. 2, which we shall discuss below.

Maxwell's paper is written in a traditional style. It consists of three parts and contains 23 clearly formulated "propositions," in each of which a definite problem is posed and solved.

In the first and particularly important part of this paper, which carries the title "On the motion and collision of perfectly elastic spheres," Maxwell considers two-body collisions of spheres having different masses and radii (which corresponds to the presence in the gas of molecules of different species). In Proposition III, Maxwell poses the problem: "Given the direction and magnitude of the velocities of two spheres before impact, and the line of centres at impact; to find the velocities after impact," (Ref. 1, p. 21 in Philos. Mag.).

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[4] The tradition preserved at Cambridge that Maxwell first derived the velocity distribution law for molecules in an examination by Stokes in 1854 can hardly correspond to reality. He evidently derived Stokes's famous theorem, which had only just been discovered by Stokes and which was included among the problems posed for the examination (see Refs. 13 and 14).

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[5] On the subject of Maxwell's terminology, see Ref. 27, pp. 119–202.

He solves this problem by means of an original geometrical construction (in the velocity space) and shows that for each sphere "the velocity after impact is compounded of the velocity of the centre of gravity, and of a velocity equal to the velocity of the sphere relative to the centre of gravity," which may with equal probability be in any direction whatever" (this equality of the probabilities was proved in advance by Maxwell in Proposition II).

Figure 1 shows Maxwell's construction (Ref. 1, p. 190). OA and OB are the velocities of the spheres before the collision, OG is the velocity of the center of mass, GN is parallel to the line of the centers at the moment of collision and necessarily lies in the plane OAB, Ga and Gb are the velocities of the spheres after the collision with respect to the center of mass, and Oa and Ob are their total velocities after the collision.

This construction for elastic two-body collisions satisfying the laws of conservation of energy and momentum is also valid for particles for which the interaction forces depend (in accordance with any law) on the distance between their centers. It was used subsequently by Maxwell himself, by Boltzmann, and by other scientists and became a common and familiar construction. It is characteristic of the way of thinking of Maxwell, who made wide use of perspicuous geometrical representations.

Maxwell draws the following fundamental conclusion: "If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision; so that after a certain time the *vis viva* will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable, though the velocity of each particle changes at every collision" (Ref. 1, p. 22). Therefore, according to Maxwell, an equilibrium characterized by a quite definite steady velocity distribution function of the particles is established in a gas. In Proposition IV (which we shall consider separately in the section The Development by Maxwell of Statistical Methods), Maxwell finds the distribution function

$$f(x) = \frac{1}{\alpha\sqrt{\pi}}e^{-x^2/\alpha^2}, \tag{1}$$

by means of which one determines the number of particles whose velocity component in a given direction lies between x and $x+dx$. (In this paper, Maxwell denotes the velocity components along three mutually perpendicular axes by x,y,z; α is a constant.)

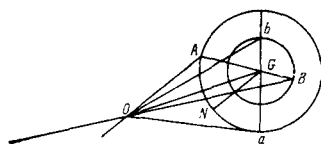By means of this function, Maxwell also obtains results important for the consideration of transport phenomena: The number of particles with velocities between v and $v+dv$ is $N(4/\alpha^2\sqrt{\pi})v^2\exp(-v^2/\alpha^2)$, where N is the total number of particles, and the mean value of the velocity is $\bar{v} = 2\alpha/\sqrt{\pi}$ and the mean square of the velocity is $\bar{v^2} = (3/2)\alpha^2$. He points out that $\bar{v^2}$ $(\bar{v})^2$, "as it ought to be."

Maxwell then solves a number of problems (Propositions V–IX) which, in particular, concern the relative velocities of particles and the approach of particles to a distance that does not exceed a given distance. In Proposition VI, Maxwell obtains an important result: For a mixture of two gases, equality of the mean kinetic energies must be established. In Proposition X, Maxwell, using the distribution function, finds the "*mean distance* travelled by each particle before striking," which is equal to $l = 1/\sqrt{2}\pi s^2 N$, where s is the distance between the centers of the particles at the time of the collision, and N is the number of particles in unit volume (as we have seen above, Clausius[44] obtained a mean free path equal to $l = 3\lambda^3/4\pi\rho^2$, from which, since $\lambda^3 = 1/N$ and $\rho = s$, we obtain $l = 3/4\pi s^2 N$ [6]).

Maxwell also determined the mean free path of two species of particle in a mixture of gases (Proposition XI).

In Proposition XII, Maxwell solved the following problem: "To find the pressure on unit of area of the side of the vessel due to the impact of the particles upon it;" he obtained the well-known formula $p = (1/3)MN\bar{v^2}$, where M is the mass of a particle and $\bar{v^2}$ is the mean square of the velocity. This result does not depend on the mean free path l, which is used in the intermediate stage of the calculation. Since, as was proved earlier, the mean kinetic energies of particles of different gases at the same temperature are equal, Maxwell concludes that "the number of particles in unit of volume, is the same for all gases at the same pressure and temperature. This result agrees with the chemical law, that equal volumes of gases are chemically equivalent." (Ref. 9, II, p. 390).

At the end of part I, Maxwell poses the very important problem of the experimental determination of "the mean length of the path of a particle between consecutive collisions" and draws attention to the investigation of internal friction as the "most direct way of doing this."

Maxwell writes: "The explanation of gaseous friction, according to our hypothesis, is, that particles having the mean velocity of translation belonging to one layer of the gas, pass out of it into another layer having different velocity of translation; and by striking against the particles of the second layer, exert upon it a tangential force which constitutes the internal friction of the gas. The whole friction between the two portions of gas separated by a plane surface, depends upon the total action between all the layers on the one side of

FIG. 1.

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[6] It should be noted that in Ref. 50 Clausius did not agree with Maxwell concerning the value of the coefficient ($\sqrt{2}$ instead of 4/3) and only many years later recognized the correctness of this coefficient in Ref. 51.

that surface upon all the layers on the other side." (Ref. 9, II, p. 390).

In Proposition XIII, Maxwell formulates the following problem: "To find the internal friction in a system of moving particles." He solves this problem by considering the transport of momentum by the particles through the plane xy, which separates layers moving along the x axis with velocity u parallel to this plane and varying linearly along the normal to it directed along the z axis. The transport depends on the mean free path. Applying the formula obtained previously for the number of particles traversing after collision the distance along the z axis from nl to $(n+dn)l$, Maxwell obtains (after integration over n from $n=0$ to $n=\infty$) for the force of internal friction the formula $F = \mu\, du/dz$, where the coefficient of internal friction,

$$\mu = \frac{1}{3}\rho l\bar{v},\qquad(2)$$

is expressed in terms of the gas density ρ, the mean free path l, and the mean velocity $\bar{v} = 2\alpha/\sqrt{\pi}$. From the values of $\sqrt{\mu/\rho}$ measured by Stokes for air, and using formula (2), Maxwell found for the first time the value of l, which was equal to $1/44700$ inch (5.68×10^{-6} cm), which has the correct order of magnitude.

Because the mean free path l is inversely proportional to the density, Eq. (2) leads us, as Maxwell writes, to "a remarkable result ... if this explanation of gaseous friction be true, the coefficient of friction is independent of the density." Maxwell regards this conslusion as "very startling."

Maxwell says that "the only experiment I have met with on the subject does not seem to confirm it." He is here evidently referring to Stokes' explanation[52] of an experiment performed by Sabine as early as 1829. According to the model proposed by Stokes, the viscosity of the gas changes with the density. As is correctly noted in the book of Ref. 24 (Book 1, p. 190–191), the correct interpretation of such experiments was given only on the basis of Maxwell's theory. The experiments made subsequently, some of them by Maxwell himself, confirmed that the coefficient of internal friction of gases does not depend on the density (see below).

In the second part of Ref. 1, "On the process of diffusion of two of more kinds of moving particles among one another," which contains Propositions XIV–XXI, Maxwell developed a theory of diffusion in gases based, like the theory of internal friction, on the notion of a mean free path, and also (in the final Proposition XXI of the second part) a theory of heat conduction. Thus, Maxwell provides a unified *theory* of all three transport processes, whereas in Ref. 44 Clausius gave only a *qualitative explanation* of the slowness of diffusion (in Ref. 44, Clausius did not consider heat conduction or internal friction).

Maxwell found the law of diffusion for the case "of two gases diffusing into each other through a plug made of a porous material" (Proposition XIX) as well as for the case of "two vessels connected by a tube" (Proposition XX). From Graham's data on experiments on the diffusion of ethylene in air,[7] Maxwell obtained the value $l \approx 1/389\,000$ inch (6.53×10^{-6} cm), which, as Maxwell's noted at the end of Ref. 1, "is not very different from that deduced from experiments on friction" (Ref. 1, p. 220). In the case of heat conduction, Maxwell concludes that "resistance of air to the conduction of heat is 10 000 000 times that of copper."

This chapter of Ref. 1 of Maxwell was the subject of criticism by Clausius, the correctness of which was recognized by Maxwell (see below).

In the third and final part of Ref. 1, "On the collision of perfectly elastic bodies of any form," Maxwell considered not only the translational motion of particles but also their rotational motion, treating the particles as rigid bodies with three principal moments of inertia. He assumes that a distribution function of the type (1) applies to the rotation around each of the three axes. Maxwell determines the motion after collision of two perfectly elastic bodies of any form if their motion before the collision and the line of the collision are given (Proposition XXII). Finally, Maxwell solves the following problem (Proposition XXIII): "To find the relations between the average velocities of translation and rotation after many collisions among bodies." He obtains the result that "the final state, therefore, of any number of systems of moving particles of any form is that in which the average *vis viva* of translation along each of the three axes is the same in all the systems, and equal to the average *vis viva* of rotation about each of the three principal axes of each particle." Thus, Maxwell obtained for the first time the law of equipartition of the kinetic energy between the translational and rotational degrees of freedom.

The expression "degree of freedom" appears much later in Maxwell's writings, in Ref. 6, in a study of the more general question of the average distribution of energy in a system of material points; see below.

Maxwell introduces the ratio β of the "whole *vis viva* to the *vis viva* of translation," i.e., the ratio of the total mean kinetic energy of the particle (translational and rotational) to the mean kinetic energy of the translational motion. He derives the formula $\beta = 2/3(\gamma - 1)$, according to which this ratio must be expressible in terms of $\gamma = c_b/c_v$ ("the ratio of the specific heat at constant volume"). On the basis of the experimental value $\gamma = 1.408$ ("well-known fact"), Maxwell obtains the value $\beta \approx 1.634$, and, since $\beta = 2$ according to his hypothesis, he regards it as proven that the proposed model of a system of particles of any shape "could not possibly satisfy the known relation between the two specific heats of all gases." With this conclusion, Maxwell concludes Ref. 1.

The formula $\beta = 2/3(\gamma - 1)$ corresponds to equipartition of the energy of a molecule between n degrees of freedom, three of which correspond to translational motion ($\gamma = c_b/c_v = (n + 2)/n$, and $\beta = n/3$, which gives this formula). For diatomic molecules with allowance

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[7] The British chemist Graham (see Ref. 53) was the first who investigated in detail the mutual diffusion of gases.

for only rotational and translational motions and for frozen vibrational motion, $n = 5$, $\gamma = 7/5 = 1.400$, and $\beta = 5/3 = 1.667$, which agrees approximately with the experimental data mentioned by Maxwell. Subsequently, Maxwell repeatedly returned to the difficulties of the theory of the specific heats of gases.

The paper of Ref. 1 served as the beginning of Maxwell's subsequent investigations on molecular physics, including experimental studies. He was particularly interested in transport phenomena. Maxwell's paper on the kinetic theory of gases in June 1860 at the meeting of the British Association, held that year in Oxford, was entitled: "On the results of Bernoulli's theory of gases as applied to their internal friction, their diffusion, and their conductivity for heat."[54]

Note that in the summary of this paper Maxwell speaks even more clearly about the contradictions in the theory of the specific heats of gases than at the end of Ref. 1: "This result of the dynamical theory, being at variance with experiment, overturns the whole hypothesis, however satisfactory the other results may be." However, despite the opinion held at that time that a single incorrect result can invalidate an entire hypothesis, Maxwell did not hold for long to such an opinion and subsequently continued to develop other consequences of the kinetic theory of gases.

In 1860, Maxwell transferred from Aberdeen (where he lost his chair as a result of the merging of two small universities) to London, to be professor of natural philosophy at King's College. At the start of his teaching at King's College, Maxwell gave an inaugural lecture[55] that reflects his broad and deep approach to the problems of physics.

The lecture indicates, in particular, Maxwell's interest in the explanation of heat as a form of mechanical motion. Maxwell writes: "... and though we cannot be said as yet to know scientifically the exact kind of motion to which such phenomena as heat and electricity are due, yet we have sufficient evidence to show that any labour we bestow in investigating such subjects by the aid of mechanical ideas will not be in vain" (Ref. 55, p.929).

Maxwell lived in London for five years, until 1865. During this period he did particularly fruitful work, in parallel with pioneering investigations on electromagnetism, on aspects of molecular physics. He regarded it as necessary to make not only theoretical but also experimental investigations and did experiments to test the "very startling" conclusion which follows from (2) for the coefficient of internal friction μ. He measured μ for air and gave the results in his paper "Cn the viscosity or internal friction of air and other gases."[56] Maxwell found that for air the value of μ at a given temperature remains constant over a wide range of pressures from 0.5 to 30 inches (from 12 to 760 mm) of mercury. At the same time, he found that μ is proportional to the absolute temperature Θ. This contradicted formula (2), according to which μ is proportional to $\sqrt{\Theta}$ (because $\sqrt{\Theta}$ is proportional to the mean velocity $\bar{v}$.

Maxwell made his experiments, which cost him much effort, by means of a specially constructed instrument, which made it possible to determine the damping of the torsional vibrations of parallel horizontal disks in air (the damping depends on the viscosity of the air, and the method was proposed by Coulomb as early as 1803). Maxwell made these experiments with his wife; subsequently, in 1877, he wrote about this in a post-card to Tait (see Ref. 12, p. 220): "My better $\frac{1}{2}$, who did all the real work of the kinetic theory is at present engaged in other researches. When she is done I will let you know her answer to your enquiry [about experimental data]." Maxwell is here referring to the participation of his wife in the experimental work on the viscosity of gases.

An experimental determination of the coefficient of internal friction of air was made independently of Maxwell in Germany by Meyer, who, in his paper "Über die innere Reibung der Gase," concluded that "the coefficient of friction changes much less rapidly with decreasing density than the density does. Therefore, Maxwell's law is at least approximately correct" (Ref. 57, p. 853). Thus, Maxwell's theory was confirmed.

Later, in 1890, in a review of the just published two-volume edition of Maxwell's scientific papers,[9] Rayleigh wrote: "... in the whole range of science there is no more beautiful or telling discovery than that gaseous viscosity is the same at all densities. Maxwell anticipated from theory, and afterward verified experimentally, that the retarding effect of the air upon a body vibrating in a confined space is the same at atmospheric pressure and in the best vacuum of an ordinary air-pump." (Ref. 58, p. 26).

In 1862, Clausius published a major theoretical paper, "Über Wärmeleitung gasförmiger Körper,"[59] in which he expressed a high estimation of Maxwell's Ref. 1. However, he did criticize individual propositions of Ref. 1, particularly those relating to the theory of the heat conduction of gases. Clausius also discovered a mistake of Maxwell in determining the numerical value of the ratio of the thermal resistivities of air and copper. He obtained the value 7000 instead of the 10 000 000 of Maxwell, who made an error on the transition from one set of units to another. Maxwell agreed with Clausius' criticism of his Ref. 1 and subsequently wrote (Ref. 2, p. 29): "I also gave a theory of diffusion of gases, which I now know to be erroneous, and there were several errors in my theory of the conduction of heat in gases which M. Clausius has pointed out in an elaborate memoir on that subject" (Maxwell gave a reference to Clausius' paper Ref. 59). It should be emphasized that Maxwell always paid attention to criticism that he recognized as correct.

In the unpublished paper "On heat conduction in gases" (see Ref. 22), written as an immediate answer to Clausius, Maxwell wrote: "Clausius recently published an investigation of a special case of heat conduction in a gas which was treated very inadequately by me in the paper (1860) to which reference has been made. I have reexamined it and have found some errors, whose influence extends to other parts of my investiga-

tion. I therefore present here my modified results only to the extent needed for understanding the necessary corrections, and I preserve the methods used in my previous paper except for the cases when I must compare them with Clausius' methods." (Ref. 22, p. 311; retranslated from the Russian because Ref. 22 is currently unavailable.)

Maxwell did not publish the corrected theory of heat conduction, presumably because he concluded that the method based on the concept of the mean free path is not applicable for the general theory of transport processes.

In 1866, in Ref. 2, Maxwell gave a more general theory of transport processes, this being no longer based on the idea of a mean free path. This is an exceptionally important and the longest of Maxwell's papers on the kinetic theory of gases. This work was done at the family estate Glenlair of the Maxwells in Scotland after he had left London in 1865. This paper, Ref. 2, was presented to the Royal Society (received May, 16, 1866 and presented on May 31), and it was then published in 1867.

Right at the start of the paper, Maxwell writes: "Theories of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules." Distinguishing between the static and dynamic molecular theories, Maxwell gives preference to the latter, according to which bodies consist of moving molecules, "even while the body is apparently at rest." This enables him to formulate very clearly the difference between solids, liquids, and gases:

"The dynamical theory supposes that the molecules of solid bodies oscillate about their positions of equilibrium, but do not travel from one position to another in the body. In fluids the molecules are supposed to be constantly moving into new relative positions, so that the same molecule may travel from one part of the fluid to any other part. In liquids the molecules are supposed to be always under the action of the forces due to neighbouring molecules throughout their course, but in gases the greater part of the path of each molecule is supposed to be sensibly rectilinear and beyond the sphere of sensible action of the neighbouring molecules" (Ref. 2, p. 27).

In the paper Maxwell proposes "to apply this theory to the explanation of various properties of gases," including "the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases."

Maxwell briefly reviews the history of the problem, beginning with "the theories of Democritus as modified by Epicurus" and expounded by Lucretius. He characterizes the work of Le Sage, Prevost, Herapath (who gave "a more extensive application of the theory of moving molecules"), and Joule (here he does not mention Krönig). Maxwell especially emphasizes the significance of Clausius' work, stating " ...his memoirs *On the kind of motion we call heat*, are a complete exposition of the molecular theory adopted in this paper."

Maxwell then speaks of his own work (Ref. 1), noting his errors (as quoted above), and, finally, mentions the work of Meyer, who "has also investigated the theory of internal friction on the hypothesis of hard elastic molecules" (Ref. 2, p. 29).

We may mention that in his historical comments Maxwell draws attention to the part of Clausius' paper Ref. 59 which lists the names of a number of scientists with whose work Clausius became acquainted after the publication of his papers Refs. 42 and 44.

Quite generally, Maxwell accorded great importance to questions of the history of science. In particular, he emphasized their importance in his inaugural lecture of Ref. 55. It is well known that in the last years of his life Maxwell devoted much time to the preparation for publication of the manuscripts of the great 18th century physicist Henry Cavendish. The world-famous experimental laboratory at Cambridge, whose first director Maxwell became in 1871, was subsequently called the Cavendish Laboratory (see, for example, Ref. 14, p. 252).

Turning to the exposition of the main material of his paper, Maxwell characterizes as follows the model of a gas which he adopts: "In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules[8] repelling one another with a force whose direction always passes very nearly through the centres of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance" (Ref. 2, p. 29).

It can be seen from this what great importance Maxwell attached to his experiments on the measurement of the viscosity of air (described in Ref. 56, see above). In the experimental investigation of internal friction, he saw a means of verifying the concepts of the molecular-kinetic theory ("dynamical theory of gases") and of obtaining information about the interaction processes of moving and colliding molecules and the properties of the molecules themselves. Maxwell points out that in a gas "the pressures in all directions are perfectly equalized only in the case of a gas at rest, but when the gas is in a state of motion, the want of perfect equality in the pressures gives rise to the phenomena of viscosity or internal friction."

Maxwell shows how "the phenomena of viscosity in all bodies may be described, independently of hypothesis," i.e., phenomenologically.

Maxwell writes the connection between the stress F and some kind of strain S in the form $F = ES$, where E is the "coefficient of elasticity for that particular kind of strain." In a solid, in the absence of viscosity, F is

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[8] This reference is to the atoms that compose the molecule.

equal to ES and $dF/dt = EdS/dt$. In a viscous body, under the assumption that the rate of decrease of F is proportional to F, we obtain

$$\frac{dF}{dt} = E\frac{dS}{dt} - \frac{F}{T}, \tag{3}$$

and for constant S

$$F = ESe^{-t/T}, \tag{4}$$

from which it can be seen that "F gradually disappears, so that if the body is left to itself it gradually loses any internal stress, and the pressures are finally distributed as in a fluid at rest."

If dS/dt is constant, "that is, if there is a steady motion of the body which continually increases the displacement,"

$$F = ET\frac{dS}{dt} + Ce^{-t/T}, \tag{5}$$

from which it can be seen that "F tends to a constant value depending on the rate of displacement."[9] Maxwell points out that ET, by which it is necessary to multiply the displacement velocity to find the force, can be called the coefficient of viscosity. This coefficient is "the product of a coefficient of elasticity, E, and a time T, which may be called the "time of relaxation" of the elastic force." Here, we have the appearance for the first time of the fundamental concept of the relaxation time as the time required for the establishment of equilibrium; it has found use in the most varied branches of physics.

Maxwell notes that in "mobile fluids," i.e., in gases, "T is a very small fraction of a second, and E is not easily determined experimentally. In viscous solids T may be several hours or days, and then E is easily measured" (Ref. 2, p.31).

For a gas "there is also a resistance to change of form, constituting what may be called the linear elasticity, or "rigidity" of the gas, but this resistance gives way and diminishes at a rate depending on the amount of the force and on the nature of the gas." Considering for a gas enclosed in a rectangular vessel with perfectly elastic walls the change in the pressure due to small changes in the lengths of the sides of the vessel, Maxwell shows that the coefficient of "rigidity" E is equal to the pressure p of the gas. "This rigidity, however, cannot be directly observed, because the molecules continually deflect each other from their rectilinear courses, and so equalize the pressure in all directions. The rate at which this equalization takes place is great, but not infinite; and therefore there remains a certain inequality of pressure which constitutes the phenomenon of viscosity." Referring to the results of his experiments (see above), according to which the coefficient of viscosity of a gas $\mu = ET = pT$ "is independent of the density, and proportional to the absolute

temperature," i.e., proportional to p/ρ, Maxwell concludes that the time of relaxation T is inversely proportional to the density and does not depend on the temperature (Ref. 2, p. 32).

It should be noted straight away that subsequent experimental investigations did not confirm proportionality of the coefficient of internal friction μ to the absolute temperature Θ (we use Maxwell's notation in Ref. 2); it was found to be proportional to Θ^r, where r = 0.65–0.96 for different gases (see Ref. 24, Book 2, p. 441). Maxwell himself subsequently recognized that r is smaller than 1 and, probably, equal to 0.77 (Ref. 5, p. 692). Nevertheless, he still continued to use a model of molecules that repel each other with a force proportional to the fifth power of the distance, since this model, which leads to $\mu \sim \Theta$, significantly simplified the calculations (see below).

Further, Maxwell emphasizes that "...the dynamical theory affords the explanation of the 'law of equivalent volumes'[10] in gases" and that "this result is true in the case of molecules acting as centres of force." Speaking of molecules as the portions of a gas "which move about as a simple body," Maxwell says "we may suppose them to be small solid bodies of a determinate form; but in this case we must assume a new set of forces binding the parts of these small bodies together, and so introduce a molecular theory of the second order." Here, Maxwell develops ideas about the structure of molecules to which he frequently subsequently returned. He also speaks of the possibility of not only rotation of the molecules as a whole but also "vibrations of various kinds" if the "parts of the body are not rigidly joined." As in Ref. 1, Maxwell uses the ratio β of the total mean energy of a molecule to the mean energy of its translational motion.

The method of investigation adopted by Maxwell consists of determining the mean values of "functions of the velocity of all the molecules of a given kind within an element of volume" (Ref. 2, p. 34). Maxwell considers for these molecules three types of mean value: (α), the mean values of the velocity components ξ, η, ζ along the coordinate axes; (β), the mean values of quadratic ("two-dimensional") functions of ξ, η, ζ (for example, ξ^2, $\xi\eta$); (γ), the mean values of cubic ("three-dimensional") functions of ξ, η, ζ (for example, ξ^3, $\xi\eta^2$).

Such mean values are encountered in the theories of diffusion (type α), the pressure of a gas and internal friction (type β), and heat conduction (type γ).

Subsequently, Maxwell determines the changes in the mean values of functions of the velocity "due, 1st, to the encounters of the molecules with others of the same system or of a different system; 2nd, to the action of external forces such as gravity; and 3rd, to the passage of molecules through the boundary of the element of volume." He applies his calculations "to the determination of the statistical cases of the final distribution of two gases under the action of gravity, the equilibrium of temperature between two gases, and the distribution

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[9] The constant C, about which Maxwell says nothing, can be determined from the condition $F = 0$ at $t = 0$, which gives $C = -ETdS/dt$, ie.,

$$F = ET\frac{dS}{dt}\left[1 - \exp\left(-\frac{t}{T}\right)\right].$$

[10] We now call it Avogadro's law.

of temperature in a vertical column." Maxwell emphasizes that these results are independent of the force law of the interaction of the molecules. He also considers transport processes: "...the dynamical cases of diffusion, viscosity, and conduction of heat, which involve the law of force between the molecules" (Ref. 2, pp. 34–35).

The main part of Maxwell's paper is devoted to a detailed exposition, using the appropriate mathematical formalism, of the listed problems, and it is hard to overestimate its significance. In his well-known studies, summarized in his "Vorlesungen über Gastheorie,"[80] Boltzmann proceeded from the methods developed by Maxwell in this paper. In what follows, we shall describe the most important problems analyzed by Maxwell from his unified point of view.

In the section "On the mutual action of two molecules," Maxwell considers the motion with respect to the center of mass of two molecules which interact in a collision ("as simple centres of force") with masses M_1 and M_2 and initial Cartesian velocity components ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2. After the collision of the molecules, these components change, but the relative velocity V remains unchanged in magnitude, the direction being merely changed through the angle 2θ. The magnitude of this angle (θ can take on values from 0 to $\pi/2$) depends on the distance b to which the molecules would approach in the absence of an interaction between them (the impact parameter in modern terminology).

Somewhat later, Maxwell calculates for the case of a repulsive force inversely proportional to the fifth power of the distance the trajectory of a molecule with respect to the force center for different values of b, gives a table, and a corresponding diagram (Fig. 2). The "impact distances" are equal to the distances between the vertical line drawn through S and the vertical asymptotes of the trajectories (these trajectories in the case of a repulsive force inversely proportional to the square of the distance are, of course, hyperbolas) (Ref. 2, p. 42).

To characterize the collisions, Maxwell introduces besides b the angle φ between the plane containing V and b (the plane of the drawing in Fig. 2) and a fixed
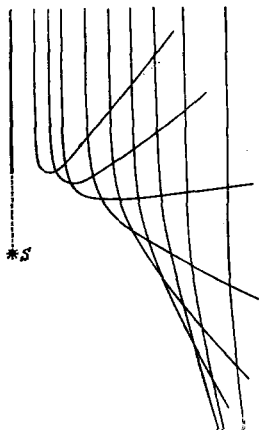

FIG. 2.

plane passing through V and parallel to the Cartesian axis x (the vertical plane passing through S and making an angle φ with the plane of the drawing) (Ref. 2, p. 38).

In the section "On the mutual action of two systems of moving molecules," Maxwell considers the interaction of molecules "of the first kind" with mass M_1 with molecules "of the second kind" with mass M_2. From the N_1 molecules of the first kind in a unit volume he considers the dN_1 molecules with velocity components between ξ_1 and $\xi_1 + d\xi_1$, between η_1 and $\eta_1 + d\eta_1$, and between ζ_1 and $\zeta_1 + d\zeta_1$, and from the N_2 molecules of the second kind in unit volume the dN_2 molecules with velocity components between ξ_2 and $\xi_2 + d\xi_2$, between η_2 and $\eta_2 + d\eta_2$, and between ζ_2 and $\zeta_2 + d\zeta_2$. For the M_1 molecules, Maxwell considers the variation δQ in time δt of any of its properties Q (which could be a velocity component or a function of the velocity components; see above) due to its interaction with an M_2 molecule. He shows that the total variation $\delta Q dN_1$ of the quantities Q per unit time for the dN_1 molecules of the first kind is equal to $(Q' - Q)Vb\,db\,d\varphi dN_1 dN_2$, where Q' is the value of Q for a molecule of the first kind after its interaction with a molecule of the second kind, V is the relative velocity (the same for all interacting pairs of M_1 and M_2 molecules), the values of b are in the interval from b to $b + db$, and the values of φ are in the interval from φ to $\varphi + d\varphi$. The finding of the mean change in Q for all the M_1 molecules reduces to integrations, first with respect to φ from 0 to 2π and with respect to b from 0 to ∞, and then with respect to $dN_2 = f_2(\xi_2, \eta_2, \zeta_2)d\xi_2 d\eta_2 d\zeta_2$ and $dN_1 = f_1(\xi_1, \eta_1, \zeta_1)d\xi_1 d\eta_1 d\zeta_1$ (f_2 and f_1 are the velocity distribution functions of the molecules of the first and second kind). This can be done if the interaction force of the molecules is a known function of the distance r between them. Under the assumption of a repulsive force inversely proportional to r^n, the integration over b of an expression of the type $(Q' - \bar{Q})Vb\,db dN_1 dN_2$ leads to the appearance of the factor $V^{\frac{n-5}{n-1}}$, which for $n = 5$(and only then) is equal to unity, the dependence on V then disappearing. This strongly simplifies all the further calculations when one is considering transport processes, and in the subsequent integration over dN_2 the integral of the type

$$\iiint QV^{\frac{n-5}{n-1}}f_2(\xi_2, \eta_2, \zeta_2)\,d\xi_2\,d\eta_2\,d\zeta_2$$

reduces to the integral

$$\iint Qf_2(\xi_2, \eta_2, \zeta_2)\,d\xi_2\,d\eta_2\,d\zeta_2 = \bar{Q}N_2,$$

where $\bar{Q}$ is the result of averaging of Q with respect to the N_2 molecules of the second kind. A similar result is obtained from the integration with respect to dN_1.

It should be emphasized that we have here the first appearance of the collision integral that was subsequently considered in detail and generalized by Boltzmann.

Before turning to the further study of the changes in Q, Maxwell gives a new and very important derivation of his velocity distribution law (1) in the special section "On the final distribution of velocity among the molecules of two systems acting on one another according to

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any law of force." We shall consider Maxwell's new proof in the section "The development by Maxwell of statistical methods," and mention here that Maxwell finds simultaneously the functions f_1 and f_2 for the molecules with masses M_1 and M_2, which immediately gives equality of the mean kinetic energies of the two kinds of molecules.

Returning in the section "Variation of functions of the velocity due to encounters between the molecules" to the determination of the variations $\delta\overline{Q}/\delta t$ of the mean values, Maxwell subsequently restricts himself to the case $n = 5$, "since it is not only free from mathematical difficulty, but is the only case which is consistent with the laws of viscosity of gases." Although, as became clear subsequently, this assertion is incorrect and it was necessary to give up the assumption $n = 5$ (the laws of interaction of molecules are more complicated and are not universal), Maxwell's general approach was very fruitful and is of considerable interest. Considering for Q the changes in the mean values due to the molecules of the first and second kind ($\delta_1 Q/\delta t$ and $\delta_2 Q/\delta t$) and an external force ($\delta_3 Q/\delta t$), Maxwell considers separately examples of the variations of quantities of the type α, β, and γ. For transport processes, it is necessary to consider general motion of all molecules, and in the section "Theory of a medium composed of moving molecules," Maxwell represents the velocity components of each molecule in the form (changing the notation)

$$u + \xi, \quad v + \eta, \quad w + \zeta,$$

where u, v, w are the components of the mean velocity of all molecules in a given element of volume at a given time, and ξ, η, ζ are the components of the relative velocity of this molecule.

Maxwell then considers the transport of the quantities Q through a plane, first in general form, and then separately for the transport of mass, momentum, and energy (cases α, β, and γ). In the resulting equations, the velocity components ξ, η, ζ and the functions of them are averaged, which gives macroscopic equations (in particular, the continuity equation), which are compared with the ordinary equations of hydrodynamics.

For the case of viscosity, Maxwell obtains the hydrodynamic Navier–Stokes equation

$$\rho \frac{du}{dt} + \frac{dp}{dt} - \mu \left(\frac{d^2 u}{dx^2} + \frac{d^2 u}{dy^2} + \frac{d^2 u}{dz^2} \right) - \frac{1}{3} \mu \frac{d}{dx} \left(\frac{du}{dx} + \frac{du}{dy} + \frac{du}{dz} \right) = \overline{X} \rho,$$

(6)

where ρ is the density, p is the pressure, and u and $\overline{X}$ are the components of the mean velocity and the external force along the x axis. Maxwell points out that "the ratio of the third and fourth terms agrees with that given by Professor Stokes," referring to Stokes' Ref. 61. Maxwell considers relaxation processes, representing the coefficient of viscosity μ in the form pT (see above).

In analyzing transport processes, Maxwell pays great attention to the diffusion of gases, carrying through the calculations to concrete results, and determines, on the basis of the experimental data of Graham, the coefficients of diffusion of various gases in air (Ref. 2, p. 61).

In connection with experimental data on viscosity, Maxwell refers to his own Ref. 56 and the work of Meyer,[57] and also Graham,[62] stating that these studies confirm μ to be independent of the density and proportional to the absolute temperature (the latter was not confirmed). From the data of his experiments on the viscosity of air at normal atmospheric pressure, Maxwell finds a relaxation time T equal to $1/5\,099\,100\,000$ second (i.e., $\approx 2 \times 10^{-10}$ sec), noting that this time is "exceedingly small" (Ref. 2, p. 71).

At the end of the paper, Maxwell considers the coefficient of thermal conductivity C and finds its relation to the coefficient of viscosity μ:

$$C = \frac{5}{3(\gamma - 1)} \frac{p_0}{\rho_0 \Theta_0} \frac{\mu}{s},$$

(7)

where $\gamma = c_p / c_V$, s is the specific weight of the investigated gas, and p_0, ρ_0, and Θ_0 are the pressure, density, and temperature of a standard gas (Ref. 2, p. 77). If $5/3$ is replaced by $5/2$ (the need for which was subsequently pointed out by Boltzmann), this formula gives good results for monatomic gases (see Ref. 25, Vol. III, pp. 16, 114, 182).

In an addendum dated December 17, 1866, "Final equilibrium of temperature," Maxwell corrects a previous error [in the section "Conduction of heat in a single medium (γ)"] and shows that a vertical column of gas "when in thermal equilibrium, has the same temperature throughout." Maxwell emphasizes that a dependence of the temperature on the height would contradict the second law of thermodynamics (Ref. 2, p. 76).

This question subsequently became the subject of a discussion between Maxwell and Gutrie (see below).

Maxwell's error was in failing to take into account the difference between $\overline{\xi^4}$ and $\overline{\xi^2 \xi^2}$. It follows from the velocity distribution law of the molecules that $\overline{\xi^4} = 3 \overline{\xi^2 \xi^2}$, and the correct result is obtained—the temperature does not depend on the height. In this connection, Maxwell wrote: "We may therefore regard this law of temperature, if true, as in some measure a confirmation of the law of distribution of velocities." (Ref. 2, p. 76).

This paper of Maxwell was the most important stage in his investigations into the kinetic theory of gases. In the following years, he remained interested in this theory, in its experimental verification, and, more generally, in questions of molecular physics and the theory of heat.

In September 1870, Maxwell gave an address to the meeting of the British Association at Liverpool on the relationship between physics and mathematics[63] (as the chairman of section A—Mathematics and Physics—of the Association). In his lecture, he paid great attention to molecular physics and the nature of molecules themselves. In particular, he said: "One of the most remarkable results of the progress of molecular science is the light it has thrown on the nature of irreversible processes" (Ref. 9, II, p. 225).

In 1871, Maxwell transferred to Cambridge, to which

he was invited as one of the leading physicists in Great Britain (at that time he was regarded as the second, after W. Thomson) to be director of the experimental physics laboratory of the Cambridge University (Cavendish Laboratory). There, Maxwell continued his investigations, combining theory with experiment. It should be emphasized that Maxwell was a skilled experimentalist.

He was also involved with teaching, in which he paid particular attention to problems of molecular physics and thermal phenomena. In October 1871, Maxwell gave an introductory lecture on experimental physics,[64] in which he said that in the coming term he intended to lecture on heat and to present "some of the evidence for the existence of molecules, considered as individual bodies having definite properties. The molecule, as it is presented to the scientific imagination, is a very different body from any of those which experience has hitherto made us acquainted" (Ref. 9, II, p. 253).

The year 1871 saw the first edition of Maxwell's textbook Theory of Heat,[7] in which he presented the science of thermal phenomena. The book begins with thermometry and calorimetry, and a major part of it is devoted to phenomenological theory, including thermodynamics. In the final chapter, he considers the "molecular theory of the structure of bodies" and there is a section in which "Maxwell's demon" appears (for more detail, see below). Maxwell systematized a great deal of material, striving to present it in a concise and elementary form without the use of higher mathematics.

After the death of Maxwell, Tait[11] wrote the following about the Theory of Heat in a paper[65] devoted to Maxwell's scientific work: "One of the few knowable things which Clerk–Maxwell did not know, was the distinction which most men readily perceive between what is easy and what is hard. What *he called* hard, others would be inclined to call altogether unintelligible. In the little book we are discussing there is matter enough to fill two or three large volumes without undue dilution (perhaps we should rather say, *with the necessary dilution*) of its varied contents" (Ref. 65, p. 320).

Maxwell's views on the molecular structure of bodies and the role of statistical methods, and on atoms and molecules were developed in his papers "Molecules"[39] and "On the dynamical evidence of the molecular constitution of bodies,"[66] in papers in the Encyclopedia Britannica ("Atom"[67] and "Constitution of bodies"[68]), and in reviews[69,70] of books by Watson[71] and Tait.[72]

In 1875, Maxwell published a paper[4] in connection with Loschmidt's experiments[73] on the determination of the coefficients of mutual diffusion for ten pairs of gases. He regarded these experiments as "most valuable and accurate." Maxwell used a theory based on a model of the collision of elastic spheres "using, however, the methods of my paper on the dynamical theory of gases (Philos. Trans. 1866) rather than those of my first pa-

per in the Philos. Mag., 1860, which are more difficult of application" (Ref. 4, p. 345). On the basis of Loschmidt's experimental data, Maxwell determined the mean free path l for a number of gases under normal conditions. He obtained for H_2, O_2, CO_2, and CO the values $l = 9.65$, 5.60, 4.82, and 4.30 (in units of 10^{-6} cm). Then Maxwell made "a few steps on more hazardous ground" and found, following Loschmidt's well-known paper "Zur Grösse der Luftmolecüle,"[74] the diameters of the molecules of these gases, obtaining the values 5.8, 7.6, 8.3, and 9.3 (in units of 10^{-8} cm). The mass of a molecule of hydrogen was found to be 4.6×10^{-24} g (instead of 3.3×10^{-24} g) and the number of molecules in 1 cm^3 (the Loschmidt number) was found to be 1.9×10^{19} (instead of 2.9×10^{19}), which at that time was a good result.

In the seventies, Maxwell published a number of other papers devoted to particular concrete problems of molecular physics.

In connection with the temperature of a vertical column of gas in equilibrium, which Maxwell had considered in Ref. 2 (see above), a discussion arose between Maxwell and Gutrie.[75-77] The latter did not agree with Maxwell's conclusion in Ref. 2 (repeated in the Theory of Heat; see Ref. 7, p. 330[12]) to the effect that the temperature of the column should not change with height. This discussion prompted Maxwell to give a new and simple proof of the general law of the Maxwell–Boltzmann distribution (in the paper Ref. 3), as a result of which the thermal equilibrium of a vertical column of gas followed as a special case. We may mention that there was also a discussion between Maxwell and Gutrie on the subject of direct and inverse collisions in a gas in equilibrium[78,79] (for more detail, see Ref. 24, Book 2, p. 346).

Maxwell was very interested in problems of diffusion. In 1876, he published the short note "Diffusion of gases through absorbing substances,"[81] in which, on the basis of molecular ideas, he analyzed diffusion in both gases and liquids.

Maxwell's response to new ideas was always lively and, in particular, he published in Nature a long review[82] of van der Waals' dissertation[83] on the continuity of the gaseous and the liquid states. Maxwell rated this investigation very high and wrote of the young scientist that "there can be no doubt that his name will soon be among the foremost in molecular science" (Ref. 9, II, p. 409). However, this did not prevent Maxwell from criticizing the manner in which van der Waals used "the very remarkable theorem of Clausius"—the virial theorem.[84] Maxwell also mentioned van der Waals in the paper of Ref. 66. In this paper, he proved for the first time that on the pV curve for the transition between the gaseous and liquid state the straight line corresponding to the transition region cuts off equal areas above and below (this rule is sometimes called Maxwell's rule).

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[11] Peter Tait was a British physicist, a friend of Maxwell, and the author of a textbook on thermodynamics which enjoyed popularity at that time.

[12] The references refer to the pagination of the 1891 edition and subsequent reprintings.
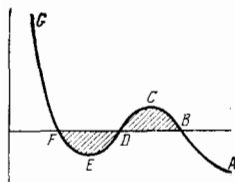
FIG. 3.

Maxwell gives the graph shown in Fig. 3 and, on the basis of the fact that at constant temperature heat cannot be transformed into work, proves that the areas of FDE and BCD must be equal (Ref. 66, pp. 105–106).

Maxwell showed very great interest in the work of Gibbs on thermodynamics. After he had become acquainted in 1873 (as he wrote to Tait; see Ref. 21) with Gibbs' papers Refs. 86 and 87 on the use of geometrical methods in thermodynamics, Maxwell made a major revision of the section on thermodynamics in Theory of Heat. In the new (4th) edition of this book, published in 1875,[7] he wrote: "Professor J. Willard Gibbs, of Yale College, U.S., to whom we are indebted for a careful examination of the different methods of representing thermodynamic relations by plane diagrams, has introduced an exceedingly valuable method of studying the properties of a substance by means of a surface." (Ref. 7, p. 195). (It should be emphasized that geometrical methods particularly appealed to Maxwell, and he used them widely in the Theory of Heat.) On the basis of Gibbs' papers, Maxwell gave a correct interpretation of entropy.

In a comment on the section "Available energy," Maxwell writes: "In former editions of this book the meaning of the term Entropy, as introduced by Clausius, was erroneously stated to be that part of the energy which cannot be converted into work. The book then proceeded to use the term as equivalent to the available energy; thus introducing great confusion into the language of thermodynamics. In this edition I have endeavoured to use the word Entropy according to its original definition by Clausius" (Ref. 7, p. 189).

Applying the geometrical method in the chapter "On the relations between the physical properties of a substance" (Ref. 7, p. 165), Maxwell considers the intersection of two isotherms with two adiabatic curves and derives the four thermodynamic relations that bear his name. He formulates these relations in the main text, and in a note writes them "in the language of differential calculus" (which he does not use in the Theory of Heat) in the form

$$\left.\begin{array}{l}\dfrac{dv}{d\theta}_{(p\,\text{const.})}=-\dfrac{d\Phi}{dp}_{(\theta\,\text{const.})}\,,\\[6pt]\dfrac{dv}{d\Phi}_{(v\,\text{const.})}=\dfrac{d\theta}{dp}_{(\Phi\,\text{const.})}\,,\\[6pt]\dfrac{dp}{dv}_{(\Phi\,\text{const.})}=\dfrac{d\Phi}{dv}_{(\theta\,\text{const.})}\,,\\[6pt]\dfrac{dp}{d\Phi}_{(v\,\text{const.})}=-\dfrac{d\theta}{dv}_{(\Phi\,\text{const.})}\,,\end{array}\right\} \qquad (8)$$

where Θ is the temperature and Φ the entropy. As is well known, the four relations (8) correspond to equality of the mixed derivatives for increments of the four thermodynamic functions (thermodynamic potential, en-

thalpy, free energy, internal energy).

It was already after the 4th edition of the Theory of Heat that Maxwell became acquainted with Gibbs' next paper on thermodynamics. This was the famous paper "On the equilibrium of heterogeneous substances"[77] (the first part was published in 1875). Maxwell wrote a special report of this paper,[88] in which he said "the methods adopted by Professor J. Willard Gibbs... seem to me to throw a new light on Thermodynamics." Maxwell gives the Gibbs condition of stable equilibrium in two of its forms (for the variation of the entropy and for the variation of the energy; see Ref. 87, p. 96). Later, Maxwell wrote a further paper[89] on Gibbs' paper Ref. 87, and in it he dwelt in more detail on Gibbs' concept of potentials (which we now call chemical potentials) as the derivatives of the energy with respect to the masses of the componenets.

It should be especially emphasized that it was in Ref. 87 that Gibbs considered the important problem of the behavior of the entropy when two identical gases and two different gases are mixed (Ref. 87, p. 227). When two different gases are mixed by diffusion, the entropy must increase, but when the gases are identical it must remain constant. However, on the basis of Avogadro's law, Gibbs concludes that the increase in the entropy is entirely determined by the number of molecules of the mixed gases "irrespective of their dynamical state and the degree of difference between them." This result, which surprised physicists, is known as the *Gibbs paradox*. It has been the subject of investigations right up to the present day (see the book of Ref. 90). It is very interesting that at the end of his paper on diffusion[81] Maxwell considers the problem of the behavior of the entropy in the case of the mutual diffusion of two identical gases and two different gases in connection with the problem of reversibility. Although there is no reference to Gibbs, there is no doubt that it was the reading of his paper which attracted Maxwell's attention to this question. Maxwell also analyzes the case of two gases "hitherto supposed to be the same," but "hereafter found to be different," and writes that in this case "the process of interdiffusion which we had formerly supposed not to be an instance of dissipation of energy would now be recognized as such an instance" (Ref. 81, pp. 645–646). Thus, Maxwell regards entropy (which increases as energy is dissipated) as a property of the system which depends on our knowledge of this system. Here, Maxwell anticipates the modern interpretation of entropy in information theory (for more detail, see Ref. 24, Book 2, p. 592).

Regarding Gibbs' work highly, Maxwell also made active propaganda for it (see Ref. 21). We may mention that in 1878, in the paper "Diagrams"[91] in the Encyclopedia Britannica, Maxwell mentioned the geometrical methods of Gibbs, which were so close to his heart. Maxwell prepared models of thermodynamic surfaces and sent one of them to Gibbs. Maxwell's opinion on Gibbs' papers was also very important for Gibbs himself (see Ref. 92). Reviewing Maxwell's work in the seventies on questions relating to molecular physics, we must mention his important paper "Capillary ac-

tion"[93] in the Encyclopedia Britannica, and also his short experimental paper on birefringence in a stream of viscous fluid.[94]

Maxwell's lectures and papers on molecular physics and allied questions published after 1870 contained much important material. However, the most important studies made by Maxwell at the end of the seventies, during the last two years of his life (1878 and 1879), are the fundamental papers of Refs. 5 and 6.

The first of these papers was devoted to the theory of transport processes in rarefied gases and laid the foundation of the theory of inhomogeneous rarefied gases.

A sufficiently detailed analysis of Ref. 5 with its complicated mathematical formalism and applications to the effects of the interaction between a rarefied gas and a surface would require a separate paper, and we shall restrict ourselves to giving a general characterization of this very interesting paper.

At the start of Ref. 5, which was published in 1879 (a brief exposition[95] appeared earlier in 1878), Maxwell writes: "In this paper I have followed the method given in my paper "On the dynamical theory of gases" (Philos. Trans., 1867, p. 49). I have shown that when inequalities of temperature exist in a gas, the pressure at a given point is not the same in all directions, and that the difference between the maximum and the minimum pressure at a point may be of considerable magnitude when the density of the gas is small enough, and when the inequalities of temperature are produced by small * solid bodies at a higher or lower temperature than the vessel containing the gas." A very important footnote is indicated by the asterisk, in which it is stated that "the dimensions of the bodies must be of the same order of magnitude as a certain length λ which may be defined as the distance travelled by a molecule with its mean velocity during the time of relaxation of the medium." "The time of relaxation—writes Maxwell further—is the time in which inequalities of stress would disappear if the rate at which they diminish were to continue constant" (see above), and he gives the formula $\lambda = 2\mu(2/\pi p\rho)^{1/2}$. "On the hypothesis that the encounters between the molecules resemble those between "rigid elastic" spheres," Maxwell obtains the formula $l = (3\pi/8)\lambda = 1.178\lambda$ for the mean free path and concludes that l can be taken "as representing what we mean by "small"." At the end of the footnote, Maxwell emphasizes: "If the force between the molecules is supposed to be a continuous function of the distance, the free path of a molecule has no longer a definite meaning, and we must fall back on the quantity λ, as defined above."

In the main part of Ref. 5, Maxwell considers, by the method developed in Ref. 2 (see above) the variations in time of mean values of functions of the velocity components of the molecules caused by collisions. He determines these mean values by means of a distribution function which takes into account deviations from spherical symmetry (see below). Further, Maxwell takes into account external forces, introduces, as in Ref. 2,

the velocity components of the macroscopic motion, and obtains equations for such motion. He finds an equation for the amounts by which the pressure of the gas along the x,y,z axes exceeds the "mean hydrostatic pressure" p. These amounts depend on the coefficient of viscosity μ and contain terms with the second derivatives of the temperature Θ with respect to the coordinates, which determine "the part of the stress which arises from inequality of temperature, which is the special subject of this paper." (Ref. 6, p. 700). The normal stress along the x axis has the form

$$p\alpha^2 = -2\mu \frac{du}{dx} + \frac{2}{3}\mu\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right)$$
$$+ 3\frac{\mu^2}{\rho\Theta}\frac{d^2\Theta}{dx^2} + \frac{3}{2}\frac{\mu^2}{\rho\Theta}\left(\frac{d^2\Theta}{dx^2} + \frac{d^2\Theta}{dy^2} + \frac{d^2\Theta}{dz^2}\right).$$

(9a)

and the tangential stress in the x,y plane is

$$p\alpha\beta = -\mu\left(\frac{du}{dy} + \frac{dv}{dx}\right) + 3\frac{\mu^2}{\rho\Theta}\frac{d^2\Theta}{dx\,dy}$$

(9b)

[here, α and β are coefficients that characterize the asymmetry of the distribution function; see below, Eq. (17)].

It should be noted that in the addenda to the main text made later, in May 1879 (the paper was presented to the Royal Society in April 1878), Maxwell gave an effective method of "applying spherical functions in the theory of gases." This method was subsequently used by Boltzmann (see Ref. 60, p. 210).

Very important is the long appendix to the paper, also dated May 1878. It is devoted to the effects of interaction of a rarefied gas with the surface of a solid which were first investigated by Crookes and then Reynolds (see Ref. 96; for more details, see Ref. 24, Book 1, p. 210, and also Ref. 97). Maxwell gives a theory of these effects associated with slipping of the gas along the surface and absorption on it of a fraction f of the molecules. The fraction $1 - f$ of the molecules is reflected, and the absorbed fraction f is then evaporated, taking the temperature of the surface. Subsequently, the coefficient f introduced by Maxwell was called the accommodation coefficient. Maxwell obtains equations that describe the interaction of a rarefield gas with a surface, and analyzes them.

Maxwell's second fundamental paper,[6] which was written shortly before his death (Maxwell died on November 5, 1879), considers Boltzmann's paper "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiallen Punkten."[98] This is indicated by the title of Ref. 6: "On Boltzmann's theorem on the average distribution of energy in a system of material points." The main, first part of this paper will be considered in detail below. We shall merely mention here that at the end of the second part of the paper (devoted to the properties of a free system with a large number of degrees of freedom) Maxwell considers for a vessel containing a mixture of gases and rotating around a vertical axis the change in the distribution of these gases under the influence of centrifugal forces, i.e., he gives a theory of the centrifuge.

4. THE DEVELOPMENT BY MAXWELL OF STATISTICAL METHODS

Maxwell's studies on the application of statistical methods in physics had an exceptionally great importance. They laid the foundations of the development of a new physical theory—statistical mechanics—and helped to form modern ideas about the nature of causality in the microscopic world.

The sources of Maxwell's interest in statistical methods are particularly important, since they help to illuminate the direction in which statistical ideas develop in Maxwell's studies.

We have already mentioned the influence on Maxwell of Clausius' paper of Ref. 44, which Maxwell read in 1859. As we have shown, this paper uses probability arguments. However, Maxwell may have been influenced by at least two further factors not directly related to Clausius' theory.

The first of these factors was Maxwell's acquaintanceship with the theory of probability and the application of probabilistic methods in different sciences. At Edinburgh, Maxwell was a close friend of Robert Campbell, a younger brother of Maxwell's first biographer, Lewis Campbell. In Lewis' opinion, it was Robert who first drew Maxwell's attention to the theory of probability (Ref. 11, pp. 127–128). In 1850, after the publication in the Edinburgh Review of Herschel's review[99] of the book of Ref. 47 by Quetelet, Maxwell acquainted himself with the application of this theory in sociology. In a letter to Lewis Campbell (Ref. 11, p. 143), Maxwell notes the use of probability in the theory of games—this subject, as it happens, was mentioned in Herschel's review—and describes the method of least squares. At Edinburgh, a teacher and friend of Maxwell was James Forbes,[13] whose scientific works the young Maxwell carefully studied (Ref. 14, p. 55). In Ref. 100, Forbes justified the reality of the existence of binary stars by means of the methods of probability theory. He lectured on this question at a meeting of the British Association, at which Maxwell too was apparently present (Ref. 23, p. 21). Boole's book An Investigation of the Laws of Thought[101] may also have been one of the sources of knowledge of probability theory for Maxwell. In this book, Boole defended the method of probability theory as a method based on solid logical principles. In addition, Maxwell may have considered the discussion of the logic of probability theory in Mill's book of Ref. 46, which he read in 1854 (Ref. 27, p. 191).

The second factor was pointed out by Garnett, who says in the biography of Maxwell that Maxwell's interest in probability theory could also be due to his study of the rings of Saturn. In his paper "On the stability of the motion of Saturn's rings,"[102] Maxwell writes: "When we encounter collisions of bodies whose number, size, and shape are unknown, we can no longer follow the mathematical laws of their motion with any certainty."

In the manuscript "Mathematical theory of the rings of Saturn" (beginning of 1860), Maxwell says: "In my previous paper I restricted myself to cases in which collisions do not occur...[but the particles] influence each other much more in collisions than by gravitational attraction.... The principle on the basis of which problems of this kind must be considered was treated by Prof. Clausius and myself" (Ref. 27, p. 92; retranslated from Russian as this reference appears to be incorrect). In the paper of Clausius, an attempt is made to treat such collisions on the basis of probabilistic considerations which, naturally, could not but attract the attention of Maxwell. It was now clear for Maxwell that the solution to the problem of Saturn's rings could be found by developing the theory of gases.

In May 1859, Maxwell wrote a letter to Stokes,[16] in which he described a theory of gases developed by himself as a result of study of the work of Clausius.[44] He noted that "of course, not all my particles have the same velocity, but the velocities are distributed in accordance with the same formulas as the errors are in the theory of least squares." Four months later Maxwell presented his theory at a meeting of the British Association in his paper "Illustrations of the dynamical theory of gases."[1]

The paper of Ref. 1 was of fundamental importance for the development of statistical physics. Essentially, it contains the first description in the history of physics of a statistical model of microscopic processes. Maxwell constructs this model on the basis of the following basic assumptions: a) all directions of motion in a gas are equally probable; b) no value of the velocity is privileged or forbidden, i.e., the velocities of the molecules are arranged in the interval from 0 to ∞; c) every gas left to itself ultimately arrives in a steady state in which a definite distribution of the velocities between the molecules is established and remains constant in time. Obviously, these assumptions are possible only when the molecules move randomly.

In Proposition IV, Maxwell formulated the problem: "To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles." Maxwell solves this problem as follows: Let N be the total number of particles, x, y, z be the velocity components of each particle with respect to three mutually perpendicular directions, and let the number of particles in unit volume of the velocity space be $Nf(x)f(y)f(z)$, where $f(x)$, $f(y)$, and $f(z)$ are functions of x, y, z that determine the distributions for the corresponding velocity components [$Nf(x)dx$ is the number of particles with velocity component between x and $x + dx$, and similar expressions are taken for the two other components]. Since the directions of the coordinate axes are chosen arbitrarily, "this number must depend on the distance from the origin alone, that is

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

Solving this functional equation, we find

$$f(x) = Ce^{Ax^2}, \quad \varphi(r^2) = C^3 e^{Ar^2}, \quad \text{(Ref. 1, p. 191)}.$$

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[13] James Forbes was in charge of the class of natural philosophy at Edinburgh University.

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If A is positive, the number of particles will increase to infinity with the velocity, and therefore Maxwell takes the coefficient A negative and equal to $-1/\alpha^2$. The constant C is found from the normalization condition. In this case, the distribution function has the form

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

In this derivation of the velocity distribution law of the molecules, Maxwell uses the assumption of statistical independence of the velocity components of an individual molecule: "the existence of the velocity x does not in any way affect that of the velocities y or z, since these are all at right angles to each other and independent." Thus, he assumes that the distribution functions $f(x)$, $f(y)$, and $f(z)$ are statistically independent of each other when the number of molecules is large, and in calculating the probabilities that the velocities of the molecules lie in the intervals from x to $x + dx$, from y to $y + dy$, and from z to $z + dz$ he multiplies $f(x)$, $f(y)$, and $f(z)$ and obtains then the correct expression for the distribution function.

Maxwell evidently assumed that the analysis made in Proposition I of the motion of the spheres after a collision—"we find that the velocities parallel to the line of centres are exactly reversed, while those perpendicular to that line are unchanged"—ensures the independence of the distributions of the velocities along three mutually perpendicular directions. Later, Maxwell recognized that his assumption is not obvious and gave a new proof for the distribution function.

Maxwell notes that "the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the "method of least squares." The velocities range from 0 to ∞, but the number of those having great velocities is comparatively small" (Ref. 9, I, p. 382). Maxwell's conclusion concerning the similarity between the distribution function and the law of the distribution of errors in the method of least squares is certainly not a chance remark but the result of his study of probability theory, which he used to derive the velocity distribution law of the molecules.

Maxwell later constructed a graphical representation to illustrate the particle velocity distribution (Ref. 66, p. 101), this being derived from the distribution of bullets over a target. The essence of the construction is as follows: To get an idea of the nature of the distribution of the velocities of the molecules in the gas, one can plot in an auxiliary diagram—the velocity diagram—from one point vectors that each represent in their direction and magnitude the velocity of a molecule. The end of the vector can be called the velocity point of the corresponding molecule. The velocity distribution of the molecules corresponds to the distribution of the velocity points in the diagram. The latter can be established in terms of a density, i.e., the number of velocity points per unit volume. The density varies from point to point in such a way that it is a function of the coordinates in the velocity diagram or, which reduces to the same thing, a function of the velocity components of the molecule. If the density is now expressed in

terms of them, the entire statistics of the molecular motion is reduced to a single formula. In the case of a steady state, any element of the velocity diagram will lose as a result of collisions as many points as it gains new ones.

Maxwell uses the obtained distribution function to find the statistical characteristics of two systems of moving particles. He determines the number of pairs (one from each system) whose relative velocity lies within a given range (Proposition V) and the number of pairs that during unit time approach to a definite distance (Proposition IX). In Proposition VI, by means of a geometrical construction that illustrates the collision of particles of two systems in a single vessel, Maxwell proves equality of the mean *vis viva* for all particles.

Proposition X poses the problem: "To find the probability of a particle reaching a given distance before striking any other." Like Clausius in Ref. 44, Maxwell assumes that this probability is equal to $e^{-\alpha x}$ if αdx is the probability of the particle's being stopped when it traverses the path dx. "The *mean distance* travelled by each particle before striking is $1/\alpha$." For α, Maxwell obtains the expression $\sqrt{2\pi}\, s^2 N$, where N is the number of particles in unit volume, and s is the distance between the centers of the particles at the time of the collision, from which it follows that the mean free path is $l = 1/\alpha = 1\sqrt{2\pi}\, s^2 N$ (see above).

This formula differs somewhat (in the value of the numerical coefficient) from Clausius' formula because Maxwell used a distribution function while Clausius took the velocities of all molecules to be the same.

Although the main aim of Ref. 1 was not the establishment of statistical laws, the development of statistical methods appeared to Maxwell to be necessary as well, since "an important physical analogy will be established, which may lead to more accurate knowledge of the properties of matter." In October 1859, Maxwell wrote to Stokes that he intended to introduce a proposition about collisions of elastic spheres independently of hypothetical assumptions about gases (Ref. 16, p. 39).

Although the distribution function made possible an essentially new approach to the explanation of phenomena in gases, it originally evoked little interest. It is possible that this reaction was due to the circumstance that the velocity distribution could not be experimentally verified.[14] The statistical description introduced by Maxwell was either ignored or rejected as incorrect.

The main criticism of the use of the velocity distribution law was made by Clausius,[59] who regarded the application of a spherically symmetric distribution function to transport phenomena as incorrect. Clausius developed his own theory, taking into account the additional kinetic energy associated with the motion of the particles in the direction of the temperature gradient,

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[14] Experimental confirmation of Maxwell's distribution law was obtained only in the twenties of this century after the development of vacuum techniques. See Ref. 103 for a discussion of experimental investigations of the velocity distribution.

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which was not taken into account by Maxwell.[15] Maxwell recognized Clausius' criticism as correct and wished to modify the distribution function by taking into account the presence of a temperature gradient, but he was not able to do this. In the Maxwell archives at Cambridge there is a rough copy of such a paper, in which he attempted to take into account the directed nature of transport processes (for more detail, see Ref. 22).

Maxwell returned to the question of the form of the velocity distribution function in 1866 in Ref. 2.

He writes: "The only case in which I have determined the form of this function is that of one or more kinds of molecules which have by their continual encounters brought about a distribution of velocity such that the number of molecules whose velocity lies within given limits remains constant. In the Philosophical Magazine for January 1860, I have given an investigation of this case, founded on the assumption that the probability of a molecule having a velocity resolved parallel to x lying between given limits is not in any way affected by the knowledge that the molecule has a given velocity resolved parallel to y. As this assumption may appear precarious, I shall now determine the form of the function in a different manner" (Ref. 2, p. 43).

The basis of the new proof is the condition of the equality of the number of direct and inverse processes for each type of collision; this has since become known as the principle of detailed balance. Maxwell considers collisions of a definite kind for which the velocity components of two colliding molecules and the collision parameters lie in definite intervals. He writes the number of such collisions in unit time in the form

$$n_1 n_2 F \, de = f_1(a) f_2(b) \, (dV)^2 \, F \, de,$$

where $n_1 = f_1(a) dV$ and $n_2 = f_2(b) dV$ are the numbers of molecules with masses M_1 and M_2 for which the velocity components a and b (before the collision) lie in intervals corresponding to the volume element dV of the velocity space (after the collision, the molecules have velocities a' and b', respectively), de depends on the ranges of variation of the parameters which characterize the given type of collision, and F is a function of the relative velocity and angle characterizing the change in the direction of this velocity as a result of the collision. Similarly, the number of collisions of molecules having velocities a' and b' before the collision and a and b after it (i.e., the number of inverse collisions in the modern terminology) is

$$f_1(a') f_2(b') \, (dV)^2 \, F' \, de.$$

The functions F and F' depend in the same manner on only the magnitude and the change in the direction of the relative velocity of the colliding molecules, and therefore Maxwell sets $F = F'$. He formulates as follows the condition for the process to be stationary: "When the

number of pairs of molecules which change their velocities from OA, OB to OA', OB'[16] is equal to the number which change from OA', OB' to OA, OB, then the final distribution of velocity will be obtained, which will not be altered by subsequent exchanges. This will be the case when $f_1(a)f_2(b) = f_1(a')f_2(b')$" (Ref. 2, p. 45). The velocities a, b and a', b' are related by

$$M_1 a^2 + M_2 b^2 = M_2 a'^2 + M_2 b'^2.$$

Solving these equations, Maxwell obtains

$$f_1(a) = C_1 e^{-a^2/\alpha^2}, \quad f_2(b) = C_2 e^{-b^2/\beta^2}, \tag{10}$$

where $M_1 \alpha^2 = M_2 \beta^2$. The constants C_1 and C_2 are determined from the normalization condition

$$\int \int \int C_1 e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi \, d\eta \, d\zeta = N_1$$

and a similar condition for C_2.

Further, Maxwell writes: "If, therefore, the distribution of velocities among N_1 molecules is such that the number of molecules whose component velocities are between ξ and $\xi + d\xi$, η and $\eta + d\eta$, and ζ and $\zeta + d\zeta$ is

$$dN_1 = \frac{N_1}{\alpha^3 \pi^{3/2}} e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi \, d\eta \, d\zeta,$$

then this distribution of velocities will not be altered by the exchange of velocities among the molecules by their mutual action: This is therefore a possible form of the final distribution of velocities. It is also the only form; for if there were any other, the exchange between velocities represented by OA and OA' would not be equal" (Ref. 2, p. 45). Maxwell emphasizes that "this final distribution of velocity is attained only when the molecules have had a great number of encounters" (Ref. 2, p. 46).

Maxwell answers Clausius' comments concerning the possibility of applying the distribution function to transport processes. "When the differential elements of the gas are changing their figure, being compressed or extended along certain axes, the values of the mean square of the velocity will be different in different directions. It is probable that the form of the function will then be

$$f_1(\xi, \eta, \zeta) = \frac{N_1}{\alpha\beta\gamma\pi^{3/2}} e^{-\left(\frac{\xi^2}{\alpha^2} + \frac{\eta^2}{\beta^2} + \frac{\zeta^2}{\gamma^2}\right)},$$

where α, β, γ are slightly different. I have not, however, attempted to investigate the exact distribution of velocities in this case, as the theory of motion of gases does not require it.

When one gas is diffusing through another, or when heat is being conducted through a gas, the distribution of velocities will be different in the positive and negative directions, instead of being symmetrical, as in the case we have considered. The want of symmetry, however, may be treated as very small in most actual cases" (Ref. 2, p.46).

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[15] Clausius always hesitated to use a distribution function. He employed Maxwell's velocity distribution function only once, in 1875 in the paper of Ref. 104.

[16] Maxwell illustrates his arguments by a diagram in which $OA = a$, $OB = b$, $OA' = a'$, $OB' = b'$.

Calculating the mean values of the various quantities ("the principal conclusions which we may draw from this investigation"), Maxwell finds that the mean value of the kinetic energy of a molecule "will be the same in each system. This is a very important result in the theory of gases, and it is independent of the nature of the action between the molecules, as are all the other results relating to the final distribution of velocities. We shall find that it leads to the law of gases known as that of Equivalent Volumes."

Maxwell understood well the importance of the results he had obtained. In the letter to Thomson[49] mentioned above, he writes: "When there are two or more kinds of molecules acting on one another by impact the average kinetic energy of a molecule is the same whatever its mass. Hence follows the dynamical interpretation of

1. Gay Lussac's law of equivalent volumes of gases.

2. Dulong and Petit's law of specific heats of gases.

I claim No. 1 but am willing to distribute as regards No. 2" (Ref. 49, p. 211).

In 1873, Maxwell published the paper "On a final state of a system of molecules in motion subject to forces of any kind,"[3] in which he generalized the results of his investigations in Ref. 1, 2 with regard to the form of the distribution function.

If an ideal gas is in a closed vessel, and no external forces act on it, the velocity distribution of the molecules satisfies the distribution function found by Maxwell, and the distribution with respect to the coordinates will be uniform and constant, i.e., the mean number of particles in any volume ΔV within the vessel will be the same. But in a field of external forces, for example, in the gravitational field of the Earth, the mean number of molecules of an ideal gas will not be the same in different parts of the vessel. In this case "the number of molecules of a given kind which, on an average, have their coordinates between x and $x + dx$, y and $y + dy$, and z and $z + dz$, and also their component velocities between ξ and $\xi + d\xi$, η and $\eta + d\eta$, and ζ and $\zeta + d\zeta$" will be described by a distribution function that depends on the coordinates and the velocity components. In the derivation of this function, Maxwell assumes that as a result of a large number of collisions there is established a steady state in which "as many pairs of molecules change their velocities from v_1, v_2 to v_1', v_2' as from v_1', v_2' to v_1, v_2" (Ref. 3, p. 352). He also assumes that not more than two molecules collide simultaneously, that a collision between molecules occurs instantaneously, and that the velocities of the colliding particles are independent.

Writing the number of molecules in the form

$$dN = f(x,\ y,\ z,\ \xi,\ \eta,\ \zeta)\ dx\ dy\ dz\ d\xi\ d\eta\ d\zeta,$$

Maxwell investigates the dependence of this expression on, first, the velocity components, and then on the coordinates.

Considering the distribution of molecules of a given kind with respect to the velocities, and using the method of argument adopted in Ref. 2, Maxwell finds that

$$f_1(\xi_1,\ \eta_1,\ \zeta_1) = C_1 e^{AM_1 v_1^2}, \quad f_2(\xi_2,\ \eta_2,\ \zeta_2) = C_2 e^{AM_2 v_2^2}. \tag{11}$$

In this case, the expressions for the number of particles can be written in the form $dN = Ce^{AM(\xi^2 + \eta^2 + \zeta^2)} d\xi d\eta \times d\zeta dx\, dy\, dz$, "where C is a function of x, y, z which may be different for different kinds of molecules, while A is the same for every kind of molecule, though it may, for aught we know as yet, vary from one place to another." Maxwell notes that "this result as to the distribution of the velocities of the molecules at a given place is independent of the action of finite forces on the molecules during their encounter, for such forces do not affect the velocities during the infinitely short time of the encounter" (Ref. 3, p. 353).

Maxwell considers further how the number of particles in the volume element $dxdydz$ changes under the influence of a force with potential ψ. In this case, "the variations of x, y, z arising from the motion of the molecules during a time δt are $\delta x = \xi \delta t$, $\delta y = \eta \delta t$, $\delta z = \zeta \delta t$, and those of ξ, η, ζ in the same time due to the action of the force, are

$$\delta \xi = -\frac{\partial \psi}{\partial x} \delta t, \quad \delta \eta = -\frac{\partial \psi}{\partial y} \delta t, \quad \delta \zeta = -\frac{\partial \psi}{\partial z} \delta t.$$

If $c = \log C$, then the change in $\log(dN/d\xi d\eta d\zeta dx dy dz) = c + AM(\xi^2 + \eta^2 + \zeta^2)$ due to the variations δx_1, δy_1, δz_1, $\delta \xi_1$, $\delta \eta_1$, $\delta \zeta_1$ is

$$\left(\xi \frac{dc}{dx} - \eta \frac{dc}{dy} - \zeta \frac{dc}{dz}\right) \delta t - 2AM \left(\xi \frac{d\psi}{dx} + \eta \frac{d\varphi}{dy} + \zeta \frac{d\psi}{dz}\right) \delta t$$
$$+ M(\xi^2 + \eta^2 + \zeta^2)\left(\xi \frac{dA}{dx} + \eta \frac{dA}{dy} + \zeta \frac{dA}{dz}\right) \delta t. \tag{12}$$

and this is equal to zero irrespective of the values of ξ, η, ζ, "since the number of molecules does not change during their motion." Hence

$$\frac{dA}{dx} = 0, \quad \frac{dA}{dy} = 0, \quad \frac{dA}{dz} = 0, \quad \text{i.e.,}$$

"A is constant throughout the whole region traversed by the molecules." Then, comparing the first and second terms in (12), Maxwell finds

$$c = AM(2\psi + B)$$

and for the number of particles of the first kind obtains finally

$$dN_1 = e^{AM_1(\xi_1^2 - \eta_1^2 + \zeta_1^2 + 2\psi_1 + B_1)}\ dx\ dy\ dz\ d\xi\ d\eta\ d\zeta, \tag{13}$$

where "A is an absolute constant, the same for every kind of molecule in the vessel, but B belongs to the first kind only." These constants can be found in terms of the total number of molecules of the given kind and the total energy of all the particles by integration with respect to the six variables.

With regard to the constant A, Maxwell notes: "The quantity A is essentially negative. Its value determines that of the mean kinetic energy of all the molecules in a given place, which is $-3/2A$, and therefore, according to the kinetic theory it also determines the temperature of the medium at that place. Hence, since A, in the permanent state of the system, is the same for every part of the system, it follows that the temperature is everywhere the same, whatever forces act upon the

molecules" (Ref. 3, p. 354).

Maxwell concludes that "the distribution of each different kind of molecules in the vessel is determined by the forces which act on them in the same way as if no other molecules were present. This agrees with Dalton's doctrine of the distribution of mixed gases" (Ref. 3, p. 354).

The law (13) was obtained for the first time by Boltzmann. In 1868–1871, in the fundamental papers "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiallen Punkten"[98] and "Über das Wärmegewicht zwischen mehratomigen Gasmolekülen,"[105] Boltzmann considered in detail Maxwell's distribution and generalized it to more complicated cases, namely, a gas in a force field and a multiatomic gas. In the first of these papers, Boltzmann showed that a multiatomic gas whose molecules can be regarded as systems of bound material points will also satisfy the Maxwell distribution law in the equilibrium state. In the second paper, Boltzmann considered the equilibrium of a gas in a potential force field and obtained as a result of a very comprehensive derivation the distribution law in the form

$$f(v_x, v_y, v_z, x, y, z)\, dx\, dy\, dz\, dv_x\, dv_y\, dv_z$$
$$= \alpha e^{-\beta\left[m\frac{v_x^2-v_y^2-v_z^2}{2}+U(x,y,z)\right]}\, dx\, dy\, dz\, dv_x\, dv_y\, dv_z,$$
$$(14)$$

where $U(x, y, z)$ is the potential energy of a molecule of the gas in the given force field, m is its mass, and β is a constant. It should be noted that Maxwell's derivation considered above [Eqs. (13) and (14) differ only in the notation] is simpler and clearer.

In 1872, Boltzmann published the paper "Weitere Studien über das Wärmegewicht unter Gasmolekülen,"[106] in which he showed that in a gas left to itself molecular collisions lead to a Maxwellian distribution of the velocities irrespective of the initial distribution. This greatly strengthened the arguments in favor of the Maxwellian velocity distribution. In the same paper, Boltzmann gave the first variant of the famous H theorem, which was to become one of the fundamental theorems of statistical mechanics.

It should however be said that these papers of Boltzmann on kinetic theory did not have a strong influence on Maxwell, who continued to go his own way. One can give two reasons for this. The first of them is, possibly, due to the circumstance that in 1866 Boltzmann attempted to give a mechanical explanation of the second law of thermodynamics, whereas Maxwell from the very start regarded the second law as a statistical law and was very critical toward all attempts to derive it from any principles of mechanics. The second reason is to be sought in the difference between the ways in which Maxwell and Boltzmann thought. Maxwell wrote to Tait in 1873: "By the study of Boltzmann I have been unable to understand him. He could not understand me on account of my shortness, and his length was and is an equal stumbling block to me" (Ref. 17, p. 114). It is perhaps for this reason that the H theorem is not mentioned once in Maxwell's papers.

At the same time, it must be emphasized that Maxwell highly regarded Boltzmann's work on the kinetic theory of gases and had great respect for Boltzmann. In 1875, in his paper "On the dynamical evidence of the molecular constitution of bodies,"[66] Maxwell notes the great importance of Boltzmann's studies for the further development of natural science: "The theorem of Boltzmann may be applied not only to determine the distribution of velocity among the molecules, but to determine the distribution of the molecules themselves in a region in which they are acted on by external forces. It tells us that the density of distribution of the molecules at a point where the potential energy of a molecule is ψ, is proportional to $\exp(-\psi/k\Theta)$, where Θ is the absolute temperature, and k is a constant for all gases. It follows from this, that if several gases in the same vessel are subject to an external force like that of gravity, the distribution of each gas is the same as if no other gas were present. This result agrees with the law assumed by Dalton, according to which the atmosphere may be regarded as consisting of two independent atmospheres, one of oxygen, and the other of nitrogen.... Another consequence of Boltzmann's theorem is, that the temperature tends to become equal throughout a vertical column of gas at rest.... But besides these results, which I had already obtained by a less elegant method and published in 1866, Boltzmann's theorem seems to open up a path into a region more purely chemical.... It is easy to see that this result ought to be applied to the theory of the states of combination which occur in a mixture of different substances. But as it is only during the present week that I have made any attempt to do so, I shall not trouble you with my crude calculations" (Ref. 66, p. 434).

It is very important that Maxwell was the first who understood the statistical origin of the second law of thermodynamics. Long before the appearance of Boltzmann's H theorem, Maxwell used his "demon" in a letter to Tait in December 1867 to illustrate the statistical origin of the second law of thermodynamics (Ref. 17, p. 213). Maxwell noted that the second law of thermodynamics applies only to systems consisting of a large number of molecules, and may be violated by individual molecules.

In the first edition of Theory of Heat[7] in 1871, in a passage about the limits of applicability of the second law of thermodynamics, Maxwell wrote: "... it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up. But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules,

opens and closes this hole, so as to allow only swifter molecules to pass from A to B, and only the slower ones to pass from B to A; He will thus, without expenditure of work, raise the temperature of B and lower that of A in contradiction to the second law of thermodynamics" (Ref. 7 pp. 308/309 in 3rd Ed.).

Maxwell's "demon" was, essentially the first important illustration of the difference between microscopic and macroscopic processes. It should be noted that Maxwell did not like the term "demon," which was proposed by Thomson; Maxwell did not wish to use physical speculations concerning the method of operation of this "demon." He proposed the use of the word "valve" (Ref. 27, p. 204). As Maxwell emphasized in a letter to Tait, his aim was "to show that the 2nd Law of Thermodynamics has only statistical certainty" (Ref. 17, p. 215).

All Maxwell's studies are organically related to each other. Complementing each other, they reflect the depth to which Maxwell penetrated into the essence of the investigated phenomena. Thus, the "demon" is needed on the one hand for the sake of its actions when a velocity distribution of the molecules is present; on the other hand, it makes the presence of the distribution function obvious; further, the study of transport phenomena is also impossible without a distribution function.

Having recognized earlier than others the qualitative differences of microscopic processes, Maxwell engaged in active propaganda for the statistical method. In a number of popular papers, he clearly formulates the features of the different methods of investigating the states of complex systems and gives preference to the statistical method when one is concerned with atoms and molecules.

In the review Ref. 69 of Watson's book A Treatise on the Kinetic Theory of Gases,[71] Maxwell notes that there are two very different methods of determining the state of complex material systems. According to the "rigorous dynamical method," we can follow each particle along its entire path and apply the laws of mechanics in all their rigor. However, "the application of this method to systems consisting of large numbers of bodies is out of the question. We therefore make use of another method which we may call the statistical method, on account of its analogy with the methods employed in dealing with the fluctuations of a large population" (Ref. 69, p. 242). Maxwell describes the features of this method as follows: "We divide the bodies of the system into groups according to their position, their velocity, or any other property belonging to them, and we fix our attention not on the bodies themselves, but on the *number* belonging at any instant to one particular group. This number is, of course, subject to change on account of bodies entering or leaving the group, and we have therefore to study the conditions under which bodies enter or leave the group, and in doing so we must follow the course of the bodies according to the dynamical method. But as soon as the process is over, when the body has fairly entered the group or left it, we withdraw our attention from the

body, and if it should come before us again we treat it as a new body, just as the turnstile at an exhibition counts the visitors who enter without respect to what they have done or are going to do, or whether they have passed through the turnstile before" (Ref. 69, p. 242).

The bodies may be grouped that are in a region of space, in accordance with their velocities, or in some other way; for example, one can consider pairs of bodies whose separations lie within certain limits.

"The object of study in the statistical method is the probable number of bodies in each group" (Ref. 69, p. 242).

In Ref. 5, Maxwell uses statistical methods to investigate the problem of the stresses in rarefied gases that arise due to inequalities of the temperature. He writes that this problem "may be stated thus: to determine the distribution of velocities among the molecules of any element of the medium, the current-velocity and the temperature of the medium being given in terms of the coordinates and the time. The only case in which this problem has been actually solved is that in which the medium has attained to its ultimate state, in which the temperature is uniform and there are no currents" (Ref. 5, p. 689), i.e., there is no macroscopic motion of the medium.

From the solution of the Boltzmann equation for such a state of the medium one obtains the spherically symmetric function

$$f_1 = A_1 e^{-h(2\psi_1 + \xi^2 + \eta^2 + \zeta^2)}, \tag{15}$$

where ψ_1 is the potential of the force with components x, y, z; A_1 is a constant, which is different for each kind of molecules; and h is a constant which is the same for all molecules and determined by the relation $\frac{1}{2}h = R\Theta$ (R is the gas constant and Θ is the temperature).

Maxwell notes that "this is the complete solution of this problem, and is independent of any hypothesis as to the manner in which the molecules act on each other during an encounter" (Ref. 5, p. 690).

For the more general case when there is an inequality of the temperatures, Maxwell takes for the molecules of a definite kind

$$dN = N \{1 + F (\xi, \eta, \zeta)\} f_0 (\xi, \eta, \zeta) d\xi\, d\eta\, d\zeta, \tag{16}$$

where "F is a rational function of ξ, η, ζ which we shall suppose not to contain terms of more than three dimensions [i.e., not more than cubic], and f_0 is the same function as in Eq. (15)" (Ref. 5, p. 691), i.e., for a homogeneous medium. Accordingly, Maxwell chooses the following function F:

$$F(\xi, \eta, \zeta) = (2h)^{1/2}(\alpha\xi + \beta\eta + \gamma\zeta) + 2h\left(\frac{1}{2}\alpha'\xi^2 + \frac{1}{2}\beta'\eta^2 + \frac{1}{2}\gamma'\zeta^2 + \beta\gamma\eta\zeta\right.$$
$$+ \gamma\alpha\zeta\xi + \alpha\beta\xi\eta) + (2h)^{3/2}\left(\frac{1}{6}\alpha''\xi^3 + \frac{1}{6}\beta''\eta^3 + \frac{1}{6}\gamma''\zeta^3 + \frac{1}{2}\alpha^2\beta\xi^2\eta + \frac{1}{2}\alpha^2\gamma\xi^2\zeta\right.$$
$$\left. + \frac{1}{2}\beta^2\gamma\eta^2\zeta + \frac{1}{2}\beta^2\alpha\eta^2\xi + \frac{1}{2}\gamma^2\alpha\zeta^2\xi + \frac{1}{2}\gamma^2\beta\zeta^2\eta + \alpha\beta\gamma\xi\eta\zeta\right),$$

$$\tag{17}$$

"where each combination of the symbols $\alpha\beta\gamma$ is to be taken as a single independent symbol, and not as a product of the component symbols" (Ref. 5, p. 693).

In the study of the influence of collisions, the averaging is performed by means of a function of the type $\{1 + F\}f_0$, where F is assumed to be small compared with unity.

The paper of Ref. 5 demonstrated once more the effectiveness of the statistical method in the solution of different problems of the kinetic theory of gases. A more general treatment of systems of strongly interacting particles was contained in Maxwell's paper "On Boltzmann's theorem on the average distribution of energy in a system of material points."[6]

The paper begins with a reference to the third section of Boltzmann's paper of Ref. 98 of 1868, which "Dr. Ludwig Boltzmann . . . has devoted . . . to the general solution of the problem of the equilibrium of kinetic energy among a finite number of material points." Noting that Boltzmann's method "is ingenious, and, as far as I can see, satisfactory," Maxwell assumes that "a problem of such primary importance in molecular science ought to be scrutinized and examined on every side, so that as many persons as possible may be enabled to follow the demonstration, and to know on what assumptions it rests" (Ref. 6, p. 713). Maxwell strives to find the most general solution to this problem, applicable to a system of any kind provided it satisfies the equations of dynamics: "I shall begin with the case in which the system is supposed to be contained within a fixed vessel, and shall afterwards consider the case of a free system . . ." (Ref. 6, p. 715).

Maxwell notes that the previous investigations in this field were based on two assumptions: "that the time during which a particle is encountering other particles is very small compared with the time during which there is no sensible action between it and other particles; and also that the time during which a particle is simultaneously within the distance of molecular action of more than one other particle may be neglected." These restrictions are "inapplicable to the theory of the equilibrium of temperature in liquids and solids, for in these bodies the particles are never free from the action of neighbouring particles." And although in the investigations of Boltzmann and Watson "it is difficult, if not impossible," to see where these conditions are used, their presence in the enunciation of the problem "cannot fail to leave in the mind of the reader the impression of a corresponding limitation in the generality of the solution" (Ref. 6, pp. 713–714).

In Maxwell's opinion, "the only assumption which is necessary for the direct proof is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy." This idea of Maxwell has a direct bearing on the "ergodic hypothesis." In fact, Maxwell proposed this hypothesis for mechanical systems that have a constant energy but are capable of interacting with their environment, in particular, with the walls of a vessel. However, he did not require this interaction to have a random nature at the microscopic level.

To present his proof of the theorem, Maxwell introduced new concepts: the "phase of the system," being the set of coordinates and momenta of the system of material points, and "the degees of freedom of the molecules" (instead of Boltzmann's "variables"). These terms are used in modern physics.

Maxwell presents his methods as follows: "I have found it convenient, instead of considering one system of material particles, to consider a large number of systems similar to each other in all respects except in the initial circumstances of the motion, which are supposed to vary from system to system, the total energy being the same in all. In the statistical investigation of the motion, we confine our attention to the *number* of these systems which at a given time are in a phase such that the variables which define it lie within given limits.

If the number of systems which are in a given phase (defined with respect to configuration and velocity[17]) does not vary with the time, the distribution of the systems is said to be *steady*.

It is shewn that if the distribution is steady, a certain function of the variables must be constant for all phases belonging to the same path. If the path passes through all phases consistent with the equation of energy, this function must be constant for all such phases. If however, there are phases consistent with the equation of energy, but which do not belong to the same path, the value of the function may be different for such phases.

But whether we are able or not to prove that the constancy of this function is a necessary condition of a steady distribution, it is manifest that if the function is initially constant for all phases consistent with the equation of energy, it will remain so during the motion. This therefore is one solution, if not the only solution, of the problem of a steady distribution.

It appears from the theorem that in the ultimate state of the system the average kinetic energy of two given 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.

Hence at a given temperature the total kinetic energy of a material system must be the product of the number of degrees of freedom of that system into a constant which is the same for all substances at that temperature, being in fact the temperature on the thermodynamic scale multiplied by an absolute constant.

If the temperature, therefore, is raised by unity, the kinetic energy is increased by the product of the number of degrees of freedom into the absolute constant" (Ref. 6, pp. 715–716).

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[17] By configuration, Maxwell means the following: "When a material system is considered from the point of view of the relative position of its parts, the set of relative positions is called configuration of the system. Knowledge of the configuration at a given instant includes knowledge of the position of each point of the system with respect to every other point at this instant (Ref. 8, p. 2; retranslated from the Russian as original currently unavailable).

Whereas Boltzmann defines the probability of the system in the phase as the ratio of the considered interval of time to the total time of the motion, taking the latter to be very long, Maxwell assumes that "there are a great many systems the properties of which are the same." Each of these systems is determined by a set of n values of the coordinates and $n-1$ momenta, and the total energy E is the same in all the systems. Maxwell considers "the number of systems which, at a given instant, are in the phase (a_1, b)."[18] Let N be the total number of systems and $N(a_1, b, t)$ be the number of systems in the phase (a_1, b) at the time t. "The aim of the statistical method is to express $N(a, b, t)$ as a function of N, of the coordinates and momenta with their limits, and of t." Setting $N(a_1, b, t) = Nf(a_2 \ldots a_n, b_1 \ldots b_n, t)da_2 \ldots da_n db_1 \ldots db_n$, Maxwell considers the motion of systems from some initial time t' to the time t and obtains the relations

$$f(a_2 \ldots t) = C(\dot{b}_1)^{-1}, \quad N(a_1, b, t) = NC(\dot{b}_1)^{-1} da_2 \ldots db_n,$$

where C is constant for all phases of the same motion. "If, however, we assume that the original distribution of the systems according to the different phases is such that C is constant for all phases consistent with the equation of energy, and zero for all phases which that equation shows to be impossible, then the law of distribution will not change with the time, and C will be an absolute constant" (Ref. 6, p. 722).

We note that Maxwell finds the statistical characteristics of the system by means of its dynamical characteristics, which he obtains from the general equations of dynamics and the energy equation. In this case, to derive the form of the distribution function Maxwell used the equation $dq_1' \ldots dq_n' dp_2' \ldots dp_n'(1/\dot{q}_1')$ $= dq_1 \ldots dq_n dp_2 \ldots dp_n(1/\dot{q}_1)$, which is obtained from dynamical considerations and is valid for systems with constant energy for the instants of time t' and t.

For the general case, when "$N(b)$ denotes the number of systems in which q_1 is between b_1 and $b_1 + db_1$, q_2 between b_2 and $b_2 + db_2$, and so on, and q_n between b_n and $b_n + db_n$, the momenta not being specified otherwise than by their being consistent with the equation of energy," it is possible to find $N(b)$ by integrating $N(a_1, b, t) = N(a_1, b)$ over $a_2, \ldots a_n$, which reduces to the calculation of

$$\int \int \int \ldots \int C(\dot{b}_1)^{-1} da_2 \ldots da_n.$$

To simplify the integration, Maxwell assumes that the variables are transformed in such a way that the kinetic energy T is expressed as a sum of squares of the momenta with coefficients that are functions of the coordinates alone.

Using the dynamical relation $b_1 = dT/da_1$, Maxwell finds that "the number of systems in a given configuration is a function of the kinetic energy corresponding to

that configuration" (Ref. 6, p. 724). For a system consisting of n' material points with masses $m_1 \ldots m_{n'}$ and $n = 3n'$ degrees of freedom, Maxwell finally obtains

$$N(b) = NC' \frac{(\Gamma(1/2))^{3n'}}{\Gamma(3n'/2)}(m_1 \ldots m_{n'})^{3/2}(2E - 2V)^{\frac{3n'-2}{2}} db_1 \ldots db_n,$$

where V is the potential function and Γ functions of $1/2$ and $3n'/2$ occur.

For a system consisting of two parts, Maxwell obtains the result that "when two parts of a system have the same temperature, the average kinetic energy corresponding to any one of the variables belonging to these parts must be the same" (Ref. 6, p. 727).

If the theory is applied to gases, for which "the parts of a system are in a great degree independent of each other" and the mean values of the potential energy of these parts "may be treated as constant," then "the variable part of the exponential function will be reduced to $\exp(-W/2K) \ldots$. We may therefore interpret the result as asserting that the density of a particular kind of gas at a given point is inversely proportional to the exponential function whose index is half the potential energy of a simple molecule of the gas at that point $[W]$, divided by the average kinetic energy $[K]$ corresponding to a variable of the system" (Ref. 6, p. 729).

This paper of Maxwell was an important step toward the creation of statistical mechanics in the generalized form that it was subsequently given by Gibbs.

5. CONCLUSIONS

The papers of Maxwell considered in the previous sections were the points of departure of a number of directions of research. Many ideas put forward in these papers (above all, in the four fundamental papers Refs. 1, 2, 5, and 6) were widely developed. Some of them have become so familiar that one usually forgets that Maxwell was their originator. This applies to the method of considering binary collisions of particles, the principle of detailed balance, and the concept of a relaxation time.

In his papers of 1868–1872 (Refs. 98, 105, 106 and others), when he began his investigations on statistical physics, and in his subsequent papers and well-known lectures on the theory of gases,[60] Boltzmann relied directly on Maxwell's papers of 1859 (Ref. 1) and especially 1866.[2] In the preface[107] to the translation of Boltzmann's lectures into English, Brush writes entirely correctly: "The foundations of the modern theory of transport were laid by Maxwell in his great memoir of 1866; it is essentially this method which Boltzmann used to make his discoveries, and which he presents in this book." The transport equation which Boltzmann derived in 1872 for the velocity distribution function, which led him to the formulation of the H theorem, is a special case of Maxwell's general kinetic equations for the transport of a quantity Q which is a function of the velocity components (as we have seen above). In his lectures, Boltzmann calls the derivation of the velocity distribution law based on consideration of direct and inverse collisions "Maxwell's proof of

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[18] The system will be in the phase (a_1, b_1) for any value of the coordinates q and momenta p if q_1 lies between b_1 and $b_1 + db_1$, q_2 between b_2 and $b_2 + db_2$, etc., p_2 between a_2 and $a_2 + da_2$, etc. The limits for p_1 are not specified, since the value of p_1 depends on the other variables.

the velocity distribution law" (Ref. 60, p. 38). Boltzmann particularly admired the way Maxwell simplified the solution of transport problems in the paper of Ref. 2 by setting $n = 5$ for repulsive forces inversely proportional to r^n (see above). Boltzmann's enthusiastic estimation of this method in a lecture dedicated to Kirchhoff (Ref. 108, p. 50) in 1887 is well known. Chapter III of the first part of the lectures of Ref. 60 carries the title "The molecules repel each other with a force inversely proportional to the fifth power of their distance" (such molecules are frequently said to be Maxwellian). Note that in the same chapter III Boltzmann uses the mathematical method of transforming spherical functions proposed by Maxwell in 1879 in the paper of Ref. 5 (in the addenda to the main text), and in chapter II of the second part of the lectures ("Physical meaning of van der Waals' theory") Boltzmann considers, following Maxwell's paper Ref. 66 of 1875, the van der Waals isotherm (the equality of the areas cut off by the horizontal straight line; see Fig. 3). In considering Liouville's theorem, Boltzmann refers to Maxwell's paper of Ref. 6 (Ref. 60, p. 340), which he highly regarded. In 1881, Boltzmann wrote a detailed review[109] of this paper. He published it in German and sent it to the Philosophical Magazine with an accompanying letter, in which he wrote: "So far as I know, this excellent paper of Maxwell's has not been reprinted in your Magazine; it may not, therefore, be without interest to your readers that some notice of it should appear, if only as an abstract . . ." (Ref. 109, p. 299). It is well known that Gibbs' statistical mechanics was a development of the ideas of Boltzmann and the ideas of Maxwell in the paper of Ref. 6.

Maxwell's ideas about the statistical origin of the second law of thermodynamics are associated with his development of statistical methods. These ideas of his include the "demon" (see above), which subsequently, in this century, has been considered by more than one generation of physicists. Smoluchowski[110] was the first who noted a possible influence of Brownian motion on a shutter; this would lead to its random opening and closing and would destroy the operation of the entire system. This would have a decisive influence on any automatic device such as a spring valve and would completely rule out the possibility of a protracted application of such a device. Szilard[111] showed for the first time in 1929 that a demon acts on information about the details of the motion of the gas and actually transforms the information into negative entropy (negentropy). Slater[112] posed the problem of the part that the uncertainty principle could play in the problem of the demon. Essentially, we are here, as Brillouin emphasizes in the book Science and Information Theory[113] (in the chapter "Maxwell's demon and the negentropy principle of information") dealing with a much more fundamental question: "Is it actually possible for the demon to see the individual atoms?" (Ref. 113, p. 215.) Brillouin gives an explanation of the resulting paradox from the point of view of information theory. He regards the action of the demon as the transformation of information into negentropy.

We may mention that the "information" approach to

problems of the statistical origin of the second law can already be found in Maxwell. In connection with the consideration of the mixing of two identical or two different gases (the Gibbs paradox, see above), Maxwell wrote in 1875 at the very end of the paper Ref. 81: "Dissipated energy is energy which we cannot lay hold of and direct at pleasure, such as the energy of the confused agitation of molecules which we call heat. Now, confusion . . . is not a property of material things in themselves, but only in the mind which perceives them" (Ref. 81, p. 646).

In 1877, considering the statistical origin of the second law (at the end of the review of Ref. 71 of Tait's book Thermodynamics[72]), Maxwell also considers the problems of fluctuations (in modern terminology). He writes that the second law of thermodynamics is "a statistical, not a mathematical truth," since this truth "depends on the fact that the bodies we deal with consist of millions of molecules, and that we can never get hold of individual molecules" (Ref. 70, p. 670). Further, Maxwell refers to the calculations of Thomson who "has shown how to calculate the probability of the occurrence within a given time of a given amount of deviation from the most probable distribution of a finite number of molecules of two different kinds in a vessel, and has given a numerical example of a particular case of the diffusion of gases." Maxwell emphasizes that for "a finite number of molecules, even if the system to which they belong contains an infinite number, the average properties of this group, though subject to smaller variations than those of a single molecule, are still every now and then deviating very considerably from the theoretical mean of the whole system, because the molecules which form the group do not submit their procedure as individuals to the laws which prescribe the behaviour of the average or mean molecule." Maxwell concludes that "the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body," that with increasing number of molecules in the group "the deviations from the mean of the whole become smaller and less frequent" and that for a sensible part of the body (i.e., for a part of macroscopic size) "the probability of a measurable variation from the mean occurring in a finite number of years becomes so small that it may be regarded as practically an impossibility." Such a calculation, writes Maxwell "belongs of course to molecular theory and not to pure thermodynamics," and shows that "the truth of the second law" corresponds to "a strong probability" but not an "absolute certainty." Finally, Maxwell notes the impossibility of deducing "the second law from purely dynamical principles, such as Hamilton's principle, and without the introduction of any element of probability."

As is well known, the statistical origin of molecular phenomena such as fluctuations and the limits of applicability of the second law were subsequently considered in detailed theoretical studies, in particular, by Smoluchowski (see Refs. 115 and 116).

It is very important that Maxwell's papers initiated

the development of transport theory in this century.

In 1905, Langevin, using the method developed by Maxwell in 1866 in Ref. 2, in his paper "Sur une formule fondamentale de la théorie cinétique"[117] solved the "problem of the diffusion of one gas in another for any type of interaction between these gases" (Ref. 117, p. 299). In the special case of Maxwellian molecules (repulsive forces inversely proportional to r^5), Langevin's results agrees with Maxwell's. For the coefficient of diffusion in the "case of elastic collisions" (for the model of perfectly elastic spheres), Langevin found a formula of which he writes: "an entirely analogous formula can be derived from the results obtained by Maxwell." Langevin refers to the paper of Ref. 1 of 1859, in which Maxwell "for the first time, in the form of an addition to the purely statistical arguments of the mean free path method, introduces dynamical conditions of the collisions between the spheres" (Ref. 117, p. 317).

Important new results on transport theory in gases were obtained in the period beginning in 1911 by the independently working Chapman and Enskog. Chapman published his first paper in 1912.[118] In it, he considered the first approximation to the complete transport theory, taking as his basis Maxwell's transport equations.

Many years later (in 1961), Chapman wrote to Brush about the origin of his studies: "In the summer of 1910 after taking the last of my mathematical examinations at Cambridge University, I asked Larmor to suggest a subject of research for me in applied mathematics. I had already started writing papers on pure mathematics. Larmor drew my attention to the work of Knudsen and Smoluchowski, and I made some extensions of their results, but never published them. But I found Maxwell's papers [2, 5 in Philos. Mag.] and did not know how many mathematicians had tried to generalize his work. Thus, with the ignorant hardihood of youth I attempted a problem that Larmor would certainly have though unfit to suggest to such a novice. It seems it is sometimes good not to know too much" (see Ref. 24, Book 2, p. 455, Note 12).

In 1911, Enskog published his paper of Ref. 119, in which he also considered the first approximation to the complete transport theory for one gas on the basis of the method proposed by Boltzmann (who developed, as we have seen above, the method that Maxwell gave in Ref. 2). Then in 1912, Enskog investigated the case of a mixture of two gases[120] and established that in the general case of non-Maxwellian molecules ($n \neq 5$) the phenomenon of thermal diffusion (diffusion due to a temperature gradient) must be observed in a mixture of gases. Chapman arrived at the same conclusion subsequently, in 1917. It should be emphasized that for Maxwellian molecules ($n = 5$) a temperature gradient does not lead to diffusion (due to the compensation of two effects), and therefore Maxwell did not note the possibility of thermal diffusion.

Subsequently, Chapman and Enskog continued to develop the theory of inhomogeneous gases. We should also mention Lennard-Jones' paper of Ref. 121 in 1923.

In 1939, Chapman and Cowling published their fundamental monograph on the theory of inhomogeneous gases,[122] in which they collected together the investigations of Chapman and Enskog (using basically Enskog's treatment). In this monograph there is an historical review with a bibliography; the review emphasizes the pioneering nature of Maxwell's papers of Refs. 2 and 5.

In 1956, Ikenberry and Truesdell published a paper (in two parts[123,124]) in which, on the basis of Maxwell's paper of Ref. 5, they developed an effective method (the method of "differential iteration") for solving transport problems. By means of this method a number of problems can be more readily solved than by the methods of Chapman and Enskog.

The paper is entitled "On the pressures and the flux of energy in a gas according to Maxwell's kinetic theory," and at the end of the second part, after the acknowledgements, Truesdell writes: "It is fitting that this appraisal should end in tribute to the magnificent genius of Maxwell. Such ideas in the present memoir as are not entirely new derive from reading and rereading Maxwell's two great analytical researches on the kinetic theory [1867, 1879].[19] Indeed, in spirit this memoir passes over all developments in the kinetic theory since 1879 and goes back for its source and inspiration to what Maxwell left us" (Ref. 124, p. 120). We see here an example of how Maxwell's ideas to stimulate fruitful investigations more than three quarters of a century after his death.

Important questions that greatly interested Maxwell were the problems of the nature of molecules and of the interatomic and intermolecular forces. In his papers and lectures, Maxwell paid great attention to these problems. In his review "Interatomic forces: from Maxwell to Schrodinger,"[125] Coulson emphasizes the great importance of Maxwell's studies in the early stage in the solution of the problems of these forces and writes: "Maxwell had almost got to the limit of what he could have done in the discussion of interatomic forces. We needed the quantum theory, with its many ramifications, before one could go any further." Coulson lists the problems advanced by Maxwell: 1) What is a molecule and what is the nature of the aggregate of atoms of which it consists? 2) What is the origin of the interatomic and intermolecular forces? 3) Why are all atoms and molecules of a given kind identical? 4) How are molecules formed?

We have briefly considered a number of the important directions of investigation due to Maxwell, and we have seen how great is the contribution that Maxwell made to the development of molecular physics and statistical methods. This contribution is comparable with his contribution to electrodynamics. It is appropriate to recall the evaluation of Maxwell's scientific work which Rayleigh made as early as 1890. Rayleigh wrote in the paper of Ref. 58 about Maxwell's studies on elec-

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[19] In a footnote at this point, Truesdell says: "I suspect that if Maxwell's notes and unpublished calculations have been preserved, they may contain much that is of value."

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tromagnetism: "There can be little doubt but that posterity will regard as Maxwell's highest achievement in this field his electromagnetic theory of light, whereby optics becomes a department of electrics." And then Rayleigh speaks of Maxwell's studies in the kinetic theory of gases: "Scarcely, if at all, less important than his electrical work was the part taken by Maxwell in the development of the Dynamical Theory of Gases." Now, at the end of the twentieth century, we can see even more clearly the grandiose contribution which Maxwell made to the development of physics (see, for example, Ref. 126).

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