# Kinetic theory — From Euler to Maxwell

Jaime Wisniak*

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

Acceptance of the kinetic theory of gases was the entrance to the development of the concepts that presently explain the structure of matter. The basic ideas of the Greek philosophers remained dormant for several centuries until Euler, Bernoulli, Herapath, Waterston, Clausius, and Maxwell, injected a sounder physical picture that led to our actual understanding of the structure of a gas.

The demise of the phlogiston and caloric theories and the acceptance of the kinetic theory of gases are three of the main events that led to our present understanding of the structure of matter. Here, we trace the development of the concepts of the kinetic theory of gases from the philosophical speculations of the Greeks, the physical analysis of Leonhard Euler (1707-1783) and Daniel Bernoulli (1700-1782), to its shaping and decisive conception by James Clerk Maxwell (1831-1879).

The kinetic theory regards a mass of gas as a collection of a great number of independently moving minute solid particles, molecules, or atoms, separated by spaces relatively large in comparison with the diameter of the particles, These entities move mostly in straight lines, except when deflected with occasional collisions with the walls of the containing vessel and with each other. The colliding particles are supposed to act upon each other only within very small distances and for very short times before and after collision, their motion being free in the intervals between such distances and times (free path). The duration of free paths is assumed to be indefinitely large as compared to the durations of the encounters and of the mutual actions. The motion as a whole is conserved by reason of the absolute elasticity of the moving particles, while the directions of the movements of the individual particles are relentlessly changed by their mutual encounters or collisions. Molecules of different gases differ in mass, but all molecules of the same gas have the same mass. The everlasting motion of the particles can be explained

assuming that the rebound by collision occurs without loss of kinetic energy or momentum. The kinetic theory interprets the pressure, or elasticity of a gas, as the aggregate of the pressures exerted by the various molecules when they collide with the boundary; only at relatively high pressures does the effect of intermolecular forces become important.

The ideal gas laws are easily deduced from this model by Newtonian mechanics, and the temperature is identified with the mean-square velocity[1]. All other conclusions from the theory grow out of these fundamental assumptions and are a direct consequence of them.

One of the original assumptions of the kinetic theory is the perfect elasticity of the molecules, a fact that was not clearly understood and gave place to much discussion. Inasmuch as no perfectly elastic solid is known, there is no basis in experience for this assumption. In actual solids, part of the kinetic energy of colliding spheres is transformed into heat due to friction in the deformation of the bodies. Nevertheless, the kinetic theory develops the notion, that, heat is the energy of molecules in motion. It follows then that no energy can be lost as heat in continuous collisions and the body must be perfectly elastic[2].

**Early ideas**

In his book *De Rerum Natura*[3] Titus Lucretius Carus (more familiarly Lucretius, *ca*. 99-55 BCE) describes in the following poetic way the atomic structure of matter and the movement of the particles: "And now, since I have taught that things cannot Be born from nothing, nor the same, when born, To

nothing be recalled…For mark those bodies which, though known to be In this our world, are yet invisible…Yet these must be corporeal at the base…Too small for eyes to see…Thus Nature ever by unseen bodies Works…All nature, then, as self-sustained, consists Of twain of things: of bodies and of void …In which they're set, and where they're moved around…Now by what motions the begetting bodies Of the world-stuff beget the varied world, And then forever resolve it when begot, And by what force they are constrained to this, And what the speed appointed unto them ..Wherewith to travel down the vast inane…For, when, in their incessancy so oft They meet and clash…Now what the speed to matter's atoms given…Entangled and enmassed, whereby at once …Each is restrained by each, and from without …Checked, till compelled more slowly to advance."

In 1716, the Swiss mathematician Jakob Hermann (1678-1733) published his book on theoretical mechanics, *Phoronomia*[4] in which he proposed the first definite measure of the heat of molecular motion. In Proposition LXXXV he wrote: Calor, caeteris paribus, est in composite ratione ex densitate corporis calidi, & duplicata ratione agitationis particularum ejusdem (Heat, in bodies of similar composition, is in the composed ratio of the density of the hot body and the square of the agitation of its particles), in other words, for the first time it was being suggested that the pressure is proportional to the density $\rho$ and the mean square velocity $(\overline{c^2})$ of the molecules. Hermann was asserting then that $P = K\rho\overline{c^2}$ where $K$ is a constant that depends only on the particular type of body.

In 1784, the Swiss mathematician and physicist George-Louis Le Sage (1724-1803) published his *Lucréce Newtonien*[5] where he proposed a mechanical gravitational theory based on the hypotheses that the whole universe was filled with very small particles (*corpuscules ultramondaines*) moving at great speed in all directions. When these particles collided with the particles forming matter, they exerted a force on the latter; if a body was alone in the space filled with corpuscles, it would be influenced equally from all sides but the resulting force would be zero, and if two bodies were present in the particle-filled space, then the density of ultramundane particles between the bodies would be lower than outside the bodies, because they shadowed for these. This inequality in particle density would push the two bodies one

against the other, in other words there would be gravity.

According to Le Sage, the size of ultramundane corpuscles was very small compared to the distance between them, their movement and motions were linear, collisions between them very rare, and their random motion could be considered to be a 'linear flow' of particles, moving in millions of directions at constant speed. The magnitude of the forces, *pushing* the bodies together, could be shown to be proportional with the product of the masses of the bodies and inversely proportional to the square of distance between them, a conclusion identical to Isaac Newton's (1642-1727) gravitational law. Assumption that the magnitude of the forces pushing the bodies together was proportional to the product of the masses required that the particles of matter, which formed the body, were discretely distributed and that there was much empty space between them.

Pierre Prevost (1751-1839) of Geneva (author of the theory of exchanges) published a book[6] which included a second treatise of Le Sage as well as one of his own, in which he attributed the pressure of gases to the impact of their molecules against the sides of the vessel, but introduced the ultramundane corpuscles to maintain the motion of the gaseous molecules[7].

Le Sage's theory had both supporters and opponents. The opposition was due to the fact that it was founded on more, partly independent hypotheses, and it was not a logical consequence of a more fundamental physical theory. The kinetic theory for molecules and the thermodynamic theories were for instance not yet developed and this meant that Le Sage's theory was almost forgotten for the next hundred years after its proposal. When the kinetic theory for molecules was developed at the end of the 19th century, Le Sage's theory was taken up to renewed analysis by such famous physicists as James Clerk Maxwell (1831-1879)[8] and William Thomson (Lord Kelvin, 1824-1907)[9]. Physical objections to Le Sage's theory were the following: If the planets moved through a space, filled with particles, they would encounter a frictional force and their temperature would rise. The problem of friction could be removed if the ultramundane corpuscles were extremely small and moved at velocities much higher than the speed of the macroscopic bodies. For the heating problem Lord Kelvin suggested that, as in the kinetic theory for molecules, to operate with three

forms of kinetic energy, *viz*. translational, rotational and vibrational. When a *gravific particle* (gravitational particle) transferred impulse to a body and thereby got a reduction in the kinetic energy, this loss of energy could be compensated for by a possible partial increase of the rotational and/or the vibrational energy, as suggested by Clausius[7].

According to John Dalton (1766-1844)[10], gases (elastic fluids) were made of particles possessing very diffuse atmospheres of caloric, having a bulk one or two thousand times that of the particle in a liquid or solid form. According to experience, the force of a mass of elastic fluid (pressure) was directly proportional to the density. Gases mixed by diffusion and once equilibrium was achieved the particles of one gas were not elastic or repulsive in regard to the particles of another gas but only to the particles of their own kind. Consequently, in a vessel containing a mixture of two gases, each acted independently upon the vessel, with its proper pressure, just as if the others were absent. The lowest particle of one gas in the mixture sustained the weight of all the particles of the same gas above it and the weight of no other. There was no movement of the particles, the particles of each gas being *ordered as lattices* of points regularly arranged, each gas having its own lattice, and the patterns being superimposed. When looking at the disposition of globular particles in a volume of pure elastic fluid it had to be perceived analogous to that of a square pile of shot, the particles disposed into horizontal strata; each four particles forming a square. When a volume of gas was put in a vessel of different volume then an intestine movement arise from the inequality.

By 1830, the wave theory of heat was being seriously considered as an alternative to, or modification of the caloric theory. The first extended discussion of heat and its nature were three papers published by André-Marie Ampère (1775-1836) between 1815 and 1835[11-13]. He began his first memoir by stating that it was well known that light was produced by the vibrations of a fluid distributed all over the space and named *ether;* afterwards he postulated that the total *vis viva* of a system was always conserved, *vis viva* being defined as "the summation of the products of the masses of all its molecules by the squares of their velocities $u$ at a given moment, and adding double the integral of the sum of the products of the forces multiplied by the differentials of the spaces described, in the direction of those forces, by each molecule, $\sum mv^2 + 2\int \sum F.dx$ "[13]. If the atoms vibrated while immersed in a fluid, they would gradually lose *vis viva* to it; if initially one atom was vibrating and the others were at rest, then the fluid would transfer some *vis viva* to these other. However, the total *vis viva* of all the atoms would decrease as waves were propagated through the fluid out of the system, unless we supposed it to be enclosed in a container of vibrators (*diapasons*), which were maintained in a state of vibration at a constant *vis viva*. Then eventually all the vibrators would approach the same *vis viva*.

Ampère defined as *particule* (particle) an infinitely small part of a body, having its same nature, so that a particle of a solid was a solid, that of a liquid a liquid, and that of a gas had the aeriform state. Particles were constituted of molecules maintained at a distance by attractive and repulsive forces; by the repulsion that established among them the vibratory movement of the intercalated ether; and by the attraction, in direct ratio to their masses and the inverse of the square of their distance. He called *atom* the material points from where these forces emanated and stated his belief that atoms were absolutely indivisible so that although space could divided infinitely, matter could not. According to Ampère, in the present state of knowledge, and leaving out of account the forces which produced the phenomena of electricity and magnet, the distance and the relative position of the particles of bodies was determined by three kinds of forces: the pressure that they supported, the repulsion between their particles produced by caloric, and the attractive and repulsive forces pertaining to each of these particles that depended upon their nature and bestowed various qualities upon bodies of different species. Ampère argued that the third of these forces was similar to the one that regulated the motions of celestial bodies. It was of much shorter range than the distance between gas particles, a claim he justified by noting that mixing of gases that did not combine chemically did not change the total volume. More than that, mixing of oxygen and hydrogen did not give place to condensation, as would have been expected if molecular attraction was significant. Ampère then adopted as a working principle that "les particules sont dans tous les gaz a une distance suffisante pour que les forces qui leur sont propres n'aient plus aucune influence sur leurs distances mutuelles" (the particles in all gases are at a sufficient

distance so that the forces which are specific to them no longer have any influence on their mutual distances)[11].

Ampère's approach is interesting, in that it represents a microscopic point of view *without* a kinetic theory of gases; the gas particles are imagined to have fixed positions, and pressure may be considered as one surface pressing against another. Since light traverses transparent bodies easily the ultimate molecules of bodies have to be separated by distances, which are infinitely *larger* than the dimensions of the molecules. For Ampère this meant that the distance between gaseous particles depended *only* on the temperature and pressure to which they were subjected. In this viewpoint, matter at rest was composed of material corpuscles arranged in such a manner that there was *no movement* in a gas, liquid, or solid. The idea of no movement is critical: The three states of matter were essentially "crystalline", their only difference was the amount of ether that separated the particles.

According to Ampère, the primitive forms recognized in crystallography were representative of the forms present in the other states (gas and liquid), with the molecules actually located in the apexes of the form. Most elementary particles were represented by tetrahedra; by combining with each other they yielded more complex geometrical shapes. This was consistent with Ampère's basic tenet that the geometric shape of the particle did not change during a change of state: "Je suis parti, pour cela, de la supposition que dans le cas où les corps passent à l'état de gaz, leurs particules seules soient séparées et écartées les unes des autres par la force expansive du calorique à des distance beaucoup plus grandes que celles où les forces de affinité et de cohésion ont une action appreciable" (I have started from the supposition that when a body passes to the gaseous state its particles become separated by the force of caloric to a distance much larger than that when the affinity and cohesion forces are important.)[13].

**The kinetic theory**

Euler, Bernoulli, John Herapath (1790-1868), and John Waterston (1811-1883) may be considered the principal scientists who prior to 1850 attempted a more or less complete mathematical treatment of gases based on a set of molecular postulates.

Euler[14] was the first to formulate a real kinetic theory. In his paper, he conceived air as made up of whirling spherical molecules closely packed together and made of a core of æther surrounded first by a layer of air and then by another layer of water. Air pressure was a manifestation of the centrifugal force associated with whirling and humidity was related to the proportion between water and air present in their respective layers. Assuming that the linear velocity $u$ associated with the rotational movement is the same for all molecules (air and water), Euler derived an equation of state connecting $P$, $\rho$, $u$ and the humidity. For dry air, which is not too dense, Euler obtained as an approximation[15].

$$P \propto \frac{1}{3}\rho u^2 \qquad \ldots(1)$$

The kinetic theory was first put into mathematical form by Bernoulli as a minor item in his book on hydrodynamics[16]. He defined as elastic fluids those that have weight and expand in every direction, unless contained. In his scheme he considered a cylinder of unit height, fitted with a movable piston having a weight equal to the force of the atmosphere and exerting a pressure $P_0$. To Bernoulli the particles enclosed in the hollow cylinder were "very minute corpuscles, which are driven hither and thither with a very rapid motion", and "practically infinite in number". The particles constituted an elastic fluid, which expanded, if the weight on the piston was removed or reduced, or it became denser if the weight was increased. He then considered what happened if the pressure was increased to a value $P$ that reduced the volume to a fraction $s$ of its original value. The compression resulted in a larger force applied to the piston because the surface density of the particles was higher and because any given particle made more frequent impacts against the piston.

Bernoulli assumed that the pressure was proportional to the surface density of the particles and inversely proportional to the mean distance between them. Assuming that the particles were spherical with a diameter $d$ and with mean distance $D$ between their centres, he derived the following equation for the ratio $P_0/P$

$$\frac{P_0}{P} = s^{\frac{2}{3}}\frac{Ds^{\frac{1}{3}} - d}{D - d} = s^{\frac{2}{3}}\frac{(D/d)s^{\frac{1}{3}} - 1}{(D/d) - 1} \qquad \ldots(2)$$

In order to determine the ratio $D/d$, he considered the situation in which the pressure was increased indefinitely until the particles were in mutual contact, in this circumstance, the volume had decreased to a

fraction $m$ of the original. Then $D/d = m^{-1/3}$ and Eq. (2) became

$$\frac{P}{P_0} = \frac{1 - m^{\frac{1}{3}}}{s - m^{\frac{1}{3}} s^{\frac{2}{3}}} \qquad \ldots(3)$$

According to Bernoulli, the experimental evidence available indicated that air could be compressed enough to make $m = 0$, so that Eq. (3) predicted that the force of compression was approximately inversely proportional to the volume. The pressure could also be increased by a rise in temperature and addition of heat increased the internal motion of the particles. As a result, increasing the velocity required a greater weight and it was "not difficult to see that the weight should be proportional to the square of this velocity because, when the velocity $u$ increases, not only the number of impacts but also the intensity of each of them increases equally. Therefore, there will be a weight, which the air will be able to hold, equal to $u^2P$ and equal to

$$P_0 = \frac{1 - \sqrt[3]{m}}{s - \sqrt[3]{m} s^2} u^2 P \qquad \ldots(4)$$

that is, $P_0 = Ku^2$, where $K$ is a dimensionless constant[16].

According to Bernoulli, Guillaume Amontons (1663-1705) was the one that discovered experimentally that at constant temperature, the pressure varied as the density, or that increases in pressure arising from equal increases in temperature were proportional to the density[17].

Bernoulli also speculated on the effect of temperature changes and claimed that increasing the pressure of a gas by heating it at constant volume led to a "more intense motion in particles of air". The pressure was proportional to the square of the velocity of the particles because as their velocity increased both the number of impacts and their intensity increased equally. His final equation became

$$\frac{P_s}{P_1} = \frac{u^2}{s} \qquad \ldots(5)$$

Pressure was thus directly proportional to the square of molecular velocity and inversely proportional to volume. Unfortunately, Bernoulli did not make the explicit identification of absolute temperature with mean-square velocity[18].

The kinetic theory as such, remained dormant until 1816 when John Herapath (1790-1868), proposed his theory, which essentially followed Bernoulli's[19] theory. According to Brush[20-22], Herapath apparently was not aware of the work of the latter, otherwise, his own theory would have been little different but, in advancing it, he might have benefited by Bernoulli's authority. By 1811, Herapath was engaged in researches on the theory of lunar motion attempting to reconcile Isaac Newton's (1642-1727) calculations with observation; his initial explanations were based on the impacts of particles of a æthereal fluid, somewhat along the lines of Le Sage. Having failed to understand the cause of these discrepancies, he turned to Newton's opinion regarding the cause of gravitation: Throughout all space, is diffused a very subtle and highly elastic medium, which Newton called æther, composed of extremely small and active particles. This medium is of the same nature as air or any other gas and can be expanded or contracted by an increase or diminution of heat or temperature, hence its variation in density might be due to the high temperature of the sun and to a lesser degree of the planets[23]. Herapath agreed that the principle of equality between action and reaction was perfectly valid when considering homogeneous bodies of the same temperature, but that this was not the case when the bodies had different composition or were at different temperatures, a difference should be observed in their attractive forces proportional to the greatness of the dissimilarity. Other things being equal, the attractive forces would be proportional to the temperature, that is, an increase in temperature would result in an augmentation of attraction[24].

Herapath believed that matter as observed was composed of hard, solid, inert atoms, indestructible, indivisible, and of different shapes and sizes. He defined as *numeratom* the number of atoms or particles distributed throughout a given space, unrelated to the density or homogeneity of the body. Regarding the nature of heat Herapath adopted the position of Francis Bacon (1561-1626) and Newton, and assumed that it consisted in the "intestinal motion" of the particles of bodies. The greater the heat, the greater the motion and the greater the expansion of the bodies affected. The quantity of heat in a body was merely the quantity of motion in one of the particles multiplied by the number of particles in the body. At this point Herapath made a turn in the wrong direction and stated that if the particles were

divided into a greater number, then the *individual quantity* of motion diminished and the temperature sinked though the *total* quantity of motion in the entire body remained unchanged. Thus, the *temperature* of a body was measured not by the quantity of motion in the whole body but by the share falling on each particle. In other words, it was not the total heat or quantity of motion that determined the body's temperature, it was the quotient of the whole motion by the number of particles in the body. Thus if we could measure the ratio of the temperature of two fixed points in the thermometric scale, as those of ice melting and water boiling, we would determine the point of *absolute cold*[25b]. Herapath would later show that the knowledge of the point of absolute cold allowed his kinetic theory to determine the velocity of sound, the laws of pressure and temperature in the atmosphere, the quantity of heat generated by a measured compression of a given quantity of air, etc. According to Brush[20-22], Herapath's explanations of these phenomena were not always completely correct, but his ideas were always ingenious[24].

From this description it is clear that Herapath supported the vibrational theory of heat and not the caloric one. Although he accepted that heat consisted in the vibratory motion of the particles of the body he added the wrong assumption that temperature was measured not by the velocity of the particles but by *their individual momentum*: two bodies, to be of the same temperature, would have to have their particles vibrating individually with the same force. It was immaterial how these vibrations were made and in which direction, the resulting motions were propagated from particle to particle throughout the body. If the vibrations were greater in one part of the body than in another, the tendency would be to an equality of vibratory force, that is, of intestine motion. To Herapath, temperature was a measure of the degree of intestine motion[24].

In Herapath's original view of the physical world, heat was the consequence of an elastic fluid and gases were composed of particles endued with the power of mutually repelling each other. Anyhow, he was unable to understand "how any intestine motion could augment or diminish this power" so that "after I had revolved the subject a few times in my mind, it struck me that if gases instead of having their particles endued with repulsive forces, subject to so curious a limitation as Newton proposed, were made up of particles or atoms, mutually *impinging* on one

another, and the sides of the vessel containing them…Such bodies I easily saw possessed several of the properties of gases; for instance, they would expand, and, if the particles were infinitely small, contract almost indefinitely; their elastic force would increase by an increase of motion or temperature, and diminish by a diminution…would generate heat by sudden compression, and destroy it by sudden rarefaction and any two, having ever so small a communication, would quickly and equally intermix[25d]." In other words, gases being in "a state of intestine mobility" had no distinctive properties, no active ones, but simply a mechanical existence of internal unrestrained motion. The *elasticity* of a gas was the force with which the gas tried to expand itself, or with which it resisted compression. It was calculated by "the amount of its action against similar and equal portions of the containing bodies" (in modern terms, pressure is the force applied per unit area, or the number of collisions per unit area and unit time.)[24].

In working out his theory of gases, Herapath met with a rather serious obstacle: "if gases are made of atoms, these must be absolutely hard, they must admit no breaking, splitting, shattering, or any impression whatever; and yet, if the gases are to maintain their elastic properties, and this property by the result of the particles mutually impinging on one another and the sides of the containing vessel, the particles or atoms, must likewise be elastic; that is, they must be soft, for elasticity, according to the ideas we have, is nothing but active softness. Therefore, it appeared to me that the ultimate atoms ought to possess two properties in direct contrariety, hardness and softness, which is manifestly impossible… by what means was it that if the parts of gases were absolutely hard, that they were reflected back into the medium from the sides of the containing vessel?"[20,21,26].

Herapath's initial answer to the question was that elasticity must spring from a different source to what was commonly believed, and that it might be a property of hardness, since, in general, the harder a body, the more elastic it is. Eventually, he changed his interpretation to one in which collisions had to be instantaneous; a perfectly elastic body had its shape changed by force, but recovered it again with energy equal to the force by which it was changed. This recovery mechanism meant that as much motion was generated in the recovery as was destroyed in the loss of the shape so that the result of the collision could be

determined by using the principle of conservation of momentum, even if it was not possible to describe what actually happened during the collision. In Herapath's words: "It may be asked by what means is it, if the parts of the gases are absolutely hard, that they are reflected from the sides of the containing vessel? This question is easily answered, if we allow heat to consist in an intestine motion of the parts of the body, for then the parts of a solid of equal temperature with a gas must have the same quantity, though they have not the same freedom of motion as the parts of a gas have; and hence the parts of the gas will have the same reflection from the sides of a vessel which they have from one another"[25e].

Herapath went on to derive the first part of the ideal gas law by considering the pressure exerted by two equal portions of the same gas in containers of different sizes, at the same temperature: "Now, because the only change that is supposed to take place is in the space which the gas occupies, the motions and collisions of a particle in the one will be similar to those of a corresponding particle in the other, and the temperature, that is in this case the velocity, being the same in each, the numbers of revolutions (going and coming back from a collision) that two corresponding particles in the two media make in a given time must be inversely proportional to the path the particles describe; that is, these paths being alike, and described with equal velocities, in the inverse sub-triplicate ratio of the spaces occupied by the equal portions of gases ($\propto 1/V^{1/3}$). But, because the elasticity of a gas is proportional to the action of its particles against a given portion of the surface of the containing body, the ratio of the elastic forces, arising from the repeated actions of equal numbers of corresponding particles in the two media, will likewise, their velocities being the same in both media, be inversely as the spaces occupied. But the number of particles of any one medium that strike against a given portion of the containing surface of one medium is to the number of particles of the corresponding stratum that strike against an equal and similar portion of the other medium; in the duplisubtriplicate ($\propto 1/V^{2/3}$) of the numeratoms (number of particles in unit volume). Therefore that ratio must be equal to the simple inverse ratio of the spaces occupied[23,25c]". Since the pressure of the gas was proportional to both $1/V^{2/3}$ and to $1/V^{1/3}$ then it had to be inversely proportional to the volume.

In more simple words, Herapath postulated that heat was motion and that the individual momentum of the particles measured its intensity (temperature). A system would then be in thermal equilibrium when all its atoms had the same momentum. Now, the pressure of a gas at constant volume was proportional to the intensity of the collisions against the walls of the container and to their frequency, the intensity of the collisions (temperature) was proportional to the momentum, and their frequency to the velocity. Hence, the pressure was proportional to the square of the momentum, that is, to the square of the temperature[20,21,25a,26]. In other words, Herapath correctly deduced that pressure is proportional to the number of particles per unit volume, ρ their mass $M$, and the square of their velocity, but failed in identifying the square of the velocity with the square of the temperature:

$$P \propto \frac{\rho T^2}{M} \qquad \qquad \ldots(6)$$

The relation that connects Herapath's true temperature and the temperature in degrees Fahrenheit $F$ is then

$$T = 1000\sqrt{\frac{448 + F}{480}} \qquad \qquad \ldots(7)$$

The factors 1000 and 448 enter in this relation because Herapath decided to make the true temperature of the ice point (32 °F) equal to 1000. The square root arises from his incorrect formation of the ideal gas law[18].

The observant reader will notice that the two main differences between Herapath's kinetic theory and the one accepted today (after Maxwell) is that Herapath stressed the conservation of average momentum (*mu*) in the collision between particles, and that he defined an absolute temperature, which is not related *linearly* to the temperature in °F (or °C). Consequently, if two fluids are mixed adiabatically Herapath's theory predicts that the final temperature will be different from the simple weighted average of the original temperatures[24].

In 1816, Herapath published his first results in the *Annals of Philosophy* as a short memoir to test the reaction of the scientific community[23]. He then elaborated his ideas in more detail and submitted a full account to the Royal Society in 1820. Davy rejected the paper because it was too speculative and

complicated and did not have sufficient experimental justification. In particular, he rejected the hypothesis of an absolute temperature implying an absolute zero of cold[27].

Herapath condensed all his findings in his two-volume book *Mathematical Principles of Natural Philosophy*[25], which he published by himself. This book gives an extensive description of the kinetic theory and its application to a wide range of subjects, for example, a discussion of Thomas Graham's (1805-1869) results on the diffusion of gases, of Victor Regnault's (1810-1878) work on the isotherms of hydrogen, and Joule's experiments on adiabatic compression.

Herapath was the first to show, more or less, that the kinetic theory can provide simple explanations for changes of state, diffusion, and the propagation of sound. While his ideas were not entirely correct, the antagonism they aroused seems to have arisen rather from the difference between the scene in which he found himself and that of a century earlier. By the 1800s, in England at least, original speculation of any kind and mathematical theory in particular were distrusted. Mechanics had been established and exhausted by Newton. Heat was explained in gross by the caloric theory and on the molecular scale by the vibratory motion of atoms within a ætherial substance, not a fit subject for mathematics[15].

Herapath's theory went into oblivion until thirty-five years later, when John James Waterston (1811-1883), James Prescott Joule (1818-1889), August Karl Krönig (1822-1879), Rudolf Julius Emanuel Clausius (1822-1888), and Maxwell entered the picture[18-20].

Waterston's (1811-1883) statement of his kinetic theory was more careful than that of Herapath, he realized that his was an idealized mathematical model, which might have some relation to the physical world[28]. Thus, he did not claim to develop the kinetic theory of a gas, but rather the theory of a medium "composed of free and perfectly elastic molecules in a state of motion which we have carefully to refrain from assimilating to any known form of matter until, by synthetical reasoning, circumstantial evidence has been accumulated sufficient to prove or render probable its identity"[28,29].

In 1845, through a friend, Waterston transmitted to the Royal Society the paper, "On the Physics of Media that are Composed of Free and Perfectly Elastic Molecules in a State of Motion"[29]. The paper was read before the Royal Society in 1846, but was rejected for publication in the Proceedings on the same grounds as those on which it had rejected Herapath's work twenty years earlier[18,29-31].

Waterston assumed the existence of a "vast multitude of small particles of matter, perfectly alike in every respect, perfectly elastic as glass or ivory…to be enclosed by elastic walls or surfaces in a space so much greater that their aggregate bulk as to allow them freely to move amongst each other in every direction. As all consideration of attractive forces is left out at present, it is obvious that each particle must proceed on a straight line until it strikes against another, or against the sides of the enclosure; that it must then be reflected and driven into another line of motion, traversing backwards and forwards in every direction, so that the intestine condition of the multitude of those that form the medium may be likened to the familiar appearance of a swarm of gnats in a sunbeam. The quality of perfect elasticity being common to all the particles, the original amount of *vis viva*, or living, acting force, of the whole multitude must for ever remain the same. If undisturbed by external action it cannot, of itself, diminish or increase, but must forever remain as unchanged as the matter that is associated with it and that it endows with activity…at each point of the medium we may thus conceive that particles are moving in every possible direction and encountering each other in every possible manner during so small an elapsed interval of time that it may be viewed as infinitesimal in respect to any sensible period"[30].

Waterston used his theory to derive Boyle's law and the perfect gas equation. In contrast to Herapath, he identified absolute temperature with the mean square molecular velocity and defined a correct absolute temperature scale. He considered a mixture of gases and deduced that the average molecular *vis viva* of all species was equal under equilibrium conditions[18].

In order to derive the gas laws, Waterston speculated on how an elastic space, weighing $n$ times more than a molecule could be supported by the consecutive impacts of such molecules striking it with a velocity $u$. It was clear that the impacts resulted in an increase or decrease in height. For a very large number of molecules (impacts) the plane would change its height by an infinitesimal distance, that is, the net result would correspond to a continuous force of upward pressure. To sustain a static equilibrium the number of impacts per unit time, $A$, had to be

$$A = \frac{gn}{2u} \qquad \qquad \ldots(8)$$

where $g$ is the acceleration of gravity.

Further analysis led to the conclusions that the elastic force of a medium, as represented by the pressure to confine it, was directly proportional to the number of molecular impacts per unit area per unit time and that the elastic force of a medium, $e$, with a constant mean molecular velocity was proportional to its density $\rho$, if $u$ or $u^2$ were constant[30].

Waterston's, next step was to calculate the change on the elasticity produced by a change in the velocity from $u$ to $mu$ (e.g, of $A$ to $mA$), at constant density. In this situation $2Au/g$ (Eq. 8) became

$$\frac{2Aum^2}{g} = nm^2 \qquad \qquad \ldots(9)$$

Equation (9) meant that the elasticity of a medium having a constant density was proportional to the mean square velocity, or *vis viva* of the medium, that is, $e \propto u^2$. Therefore, when both the density and the *vis viva* were changed then the elasticity had to be proportional to their product, or absent. Comparison with the ideal gas laws required that the square of the velocity, $u^2$, represented the temperature of the gas. Unlike Herapath, Waterston's theoretical model did not conflict with the possibility of perfectly elastic atoms. This possibility gave a sounder basis for his calculations[30].

William John Rankine (1820-1872) criticized Waterston's theory on the basis that the total heat of a gas could not be accounted for by translational motion of the particles and suggested remedying this defect with his own theory of rotating molecular vortices[31]. Rudolf Julius Emanuel Clausius (1822-1888) noted the same difficulty and suggested instead that the molecules of gases are composed of two or more atoms[32]. In general, although the total kinetic energy would be distributed in some way between the translational motion of the whole molecules and the internal vibratory or rotary motion of the constituents of the molecules, the translational motion of the whole molecules would always have a constant relation to the internal movements of the constituents[20,22].

August Karl Krönig (1822-1879) is usually credited with reviving the kinetic theory after 1850 and motivating the further developments of Clausius and Maxwell. In a short paper published in 1856[33], he assumed that the molecules of a gas did not oscillate about definite positions of equilibrium but moved with constant velocity in right lines until they stroke other molecules, or some surface, which was impermeable to them. He then proceeded to show how the gaseous laws could be deduced from this assumption. As stated by Brush[34] Krönig's paper represented no real advance over the work of Herapath and Joule, though it was conceived independently. Its favourable reception was due primarily to the fact that the mechanical theory of heat had been experimentally established, and also to the fact that Krönig was important enough for other scientists to pay attention to him (Professor in the *Realschule* of Berlin and an influential member of the *Physikalische Gessellschaft* of Berlin).

Clausius[32] criticized Krönig's claiming that unless collisions between molecules were central and rectilinear they would also result in rotary motion. In addition, he believed that intramolecular vibrations also took place; in a molecule consisting of several atoms these were movable to a certain extent, without separating from the main body. In gases having a complex structure the total heat could not be accounted by the *vis viva*, hence it was necessary to assume motions of another kind.

Clausius made three important contributions to the kinetic theory of gases[32,35-37]: first, calculation of number of collisions in a given volume of gas (Clausius, 1857), second, the concept of mean free path[33], which Maxwell used to give a simple explanation of transport processes; and third, the virial theorem[37], which was the basis for later work on the effect of interatomic forces on the pressure-volume temperature relationship (i.e., the equation of state, particularly that of van der Waals). He also investigated the partition energy and the ratio of specific heats of a gas; he found that the ratio of he specific heat at constant pressure to that of the constant volume should be 5/3 for a monatomic gas[34].

In one of his first papers on the subject Clausius[32] calculated the relation between the pressure generated by the collisions in a gas and the motion of the particles. Since this relation was not connected to the shape of the containing vessel he selected one formed by two parallel plates of area $A$, separated by a distance $\delta$ negligible in relation to the other dimensions. In addition, he assumed that all the $n$ particles, each having mass $m$, moved at a certain *mean* velocity, chosen in such a way that the total *vis*

*viva* of all molecules was the same as that corresponding to their actual velocities. Clausius reasoning is as follows: if the molecules approach the surface at an angle $\theta$ and velocity $u$, then the number of impacts on a given side is $(u\cos\theta)/2\delta$. Since, on an average, each direction should be equally represented, then the number of shocks imparted by all the molecules located in the range $\theta$ to $\theta + d\theta$ is $(nu/2\delta)\cos\theta \sin\theta d\theta$ and the quantity of motion imparted to these molecules by a face of the vessel in the unit of time, is $(nmu^2/\delta)\cos^2\theta \sin\theta d\theta$. Integrating the last relation between the limits $\theta = 0$ and $\theta = \pi/2$ yielded $nmu^2/3\delta$. For a plate of area $A$ the pressure exerted will be $P = nmu^2/3v$, where $v = \delta A$, so that $nmu^2/2 = (3/2) P$. Comparison of the latter relation with the equation of state for an ideal gas indicates that the *vis viva* of the translational movement is proportional to the absolute temperature.

Clausius then derived the following expression for the velocity of the molecules at the temperature of melting ice (273 degrees):

$$u = 485\left[\frac{T}{(273\rho)}\right]^{1/2} \qquad \ldots(10)$$

where $T$ is the absolute temperature and $\rho$ the density in kg/m$^3$. From Eq. (10), Clausius calculated the velocities of molecules of oxygen, nitrogen, and hydrogen as 461, 492, and 1844 m/s, respectively. In this paper, Clausius mentions that he was aware that Joule had recently calculated the velocity of hydrogen molecules[38], but that he did not know the value reported by Joule (1846 m/s).

In a later paper Clausius derived the virial theorem[36]

$$\frac{1}{2}\sum mc^2 = \frac{3}{2}Pv + \frac{1}{2}\sum\sum Rr \qquad \ldots(11)$$

where the last term represents the virial of the force (force due to the internal actions of the particles of the system).

It is clear that Clausius analysis led to a bridge between the atomic theory and thermodynamics; he perceived not only that the atomic theory could thus be used to explain macroscopic thermodynamics, but also that experimental data on thermal properties could be translated into specific statements about the nature of atoms themselves[34].

In 1860, Maxwell published his first paper on the kinetic theory in which he introduced his celebrated law for the distribution of molecular velocities[39].

Contrary to Clausius Maxwell's basic hypothesis that the collisions between molecules in a gas tended to produce an *array* of velocities whose statistical distribution had a known probability, he asserted that the velocity components of molecules in different directions could be treated as independent random variables. His only justification of this assumption was the fact that if two elastic spheres collide, all directions of rebound are equally likely. He apparently believed that this fact would ensure not only that all directions of motion are equally probable in a gas, but also that the probability distribution for each component of the velocity is independent of the values of the other components[26].

As described by Jeans and Hille[40], Maxwell assumed that although the molecules of a gas are moving in different ways, they can be divided up into a system of showers, such that all the molecules in any one shower have approximately the same velocity and are moving in the same direction. Let $u$, $v$, $w$ denote the components of the velocity of any molecules in three directions at right angles in space, and let us fix our attention on any one shower whose molecules have components $u_1$, $v_1$, and $w_1$. Let us consider the impact of the molecules of this shower upon an area $S$ of the boundary of the containing vessel, and for simplicity let $S$ be perpendicular to the direction of $u$. Then, each molecule of the shower that strikes the area gives up momentum $mu$ to it before its motion in the $u$ direction is arrested, and as it rebounds with equal velocity, it also acquires momentum $mu$ in the opposite direction, so that the total transfer of momentum is $2mu$. The number of molecules belonging to the shower which strike the area $S$ in a small interval of time $dt$ is equal to the number of molecules that lay within a distance $u_1dt$ of $S$ at the beginning of this interval and so occupy a small disk of volume $Su_1dt$ of the gas. If there are $v_l$ molecules in a unit volume belonging to the shower, the number of molecules inside the disk is $Su_1v_1dt$. Thus, these molecules transfer momentum $2mu_1^2v_1Sdt$ to the area $S$ of the boundary. The total momentum transferred by the molecules of all showers is $2mSdt\sum v_i u_i^2$, where the sum includes a term for each shower whose molecules are moving with a component $u$ directed toward $S$. The sum can also be written $\frac{1}{2}vu^2$, where $v$ is the total number of molecules in unit volume and $U^2$ denotes the *average*

value of $u^2$ for the different molecules. The factor 1/2 is introduced because half of all the showers can be moving with a component $u$ directed away from $S$ and hence cannot contribute to the pressure of $S$. Let $\overline{c^2}$ stand for the average value of ($u^2 + v^2 + w^2$), or the square of the actual velocity, for all the molecules. Since as many molecules will be moving in one direction as in another, the average value of $u^2$, $v^2$, and $w^2$ will be the same. Hence $U^2 = \frac{1}{3}\overline{c^2}$ and the momentum transferred to the area $S$ during the interval $dt$ is $\frac{1}{3}mvS\overline{c^2}dt$. The momentum transferred is also equal to $PSdt$, where $P$ is the pressure or force per unit area on the boundary, so that[40],

$$P = \frac{1}{3}mv\overline{c^2} \qquad \qquad …(12)$$

Since $mv$ is the total mass in unit volume ($\rho$) expressed in grams per cubic centimetre, we have[40].

$$P = \frac{1}{3}\rho\overline{c^2} \qquad \qquad …(13)$$

Since $P$ and $\rho$ can be measured for any gas, the value of $\overline{c^2}$ can be calculated. $c$ is called the *root-mean square velocity* of the molecules; the pressure would be the same as it actually is, if all the molecules were moving with the velocity $c$[40].

As stated above, Maxwell assumed that the molecules of a gas are not moving with the same velocity. When the gas is at rest and free from disturbance, the effect of collisions between its molecules was shown by Maxwell to be such that the molecular velocities soon become distributed in a definite manner. The gas is then is a steady or normal state. When this state has been attained, the statistical equilibrium is actually maintained in a very simple manner. Let us divide all possible velocities into distinct ranges $a,b,c,…$When two molecules moving with velocities $a$, $b$ collide, the collision changes the motion of both and they assume new velocities $p$, $q$. Thus, the collision takes one molecule away from each of the classes $a$, $b$ and adds one to each of the classes $p$, $q$. When the gas is in its steady state, there occur just as many collisions of the inverse type, in which a molecule is taken from each of the classes $p$, $q$ and added to one of the classes $a$, $b$. The statistical effect of the collisions is thus nil[40].

Maxwell, proved that the number of molecules for which the component $u$ of its velocity lies between $u$ and $u + du$ is given by

$$N\left[\frac{hm}{\pi}\right]^{0.5}exp[-hmc^2]du \qquad …(14)$$

where $N$ is the total number of molecules and $h$ is a constant, which was found to depend on the temperature. Equation (14) represents what is commonly known as *Maxwell's law of distribution of velocities*[40].

In a similar way, the total velocity of a molecule was shown to be given by

$$4\pi N\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}exp\left[-hmc^2\right]c^2dc \qquad …(15)$$

Integration of Eq. (14) leads to the result that the average of the square of the velocity, $\overline{c^2}$, is also equal to $3/2hm$[40].

Since $m\overline{c^2}/2$ also equals $3kT/2$ in terms of the Boltzmann constant $k$ and the absolute temperature $T$, it follows that[40]

$$h = \frac{1}{2kT} \qquad \qquad …(16)$$

Maxwell also showed that a system of hard spheres would have a viscosity independent of density and proportional to the square root of the absolute temperature. The experimental confirmation of the first of these predictions by Maxwell himself and by many other investigators helped to establish the kinetic theory[22].

Maxwell prefaced his own papers with short historical accounts of the theory's development. In his paper *Illustrations of the Dynamical Theory of Gases*, read at the British Association meetings in Aberdeen in 1859, he mentioned that Bernoulli, Herapath, Joule, Krönig, Clausius, etc. had shown that the relation between pressure, temperature and density in a perfect gas can be explained by supposing the particle to move with uniform velocity in straight lines, striking against the side of the containing vessel and thus producing pressure. Maxwell recognized Herapath as a precursor of his own research in kinetic theory and gave the following assessment of Herapath's work: "His theory of the collision of perfectly hard bodies, such as he supposed the molecules to be, is faulty… This author, however, has applied his theory to the numerical results of experiment in many cases, and his speculations are always ingenious, and often throw much real light in the questions treated. In

particular, the theory of the temperature and pressure and gases and diffusion are clearly pointed out[39]. This paper also remarked that Clausius had determined the mean length of the path in terms of the average distance of the particles and the distance between the centres of two particles when collisions take place[7].

The whole subject was put on a more rigorous mathematical basis by the work of Ludwig Boltzmann (1844-1906), who investigated the velocity distribution in a non-uniform gas. He derived an integro-differential equation for the distribution function, whose solution would permit one to calculate all the transport coefficients, viscosity, thermal conductivity, and diffusion. While Boltzmann never managed to obtain a satisfactory solution for this equation in the most general case, he did show that two important results could be extracted from it: (a) once Maxwell's equilibrium distribution is established in a gas, it is not changed by molecular collisions; (b) a quantity called $H$, depending on the distribution function, can never increase in the course of time. By identifying $H$ with minus the entropy of the system, Boltzmann thus found a microscopic proof of the second law of thermodynamics – the $H$ theorem[22].

### Epilogue

On his Presidential Address to the British Association, read at Edinburgh, on August 2, 1871, Thomson brought in the kinetic theory in this words[41]: "The greatest achievement yet made in molecular theory of the properties of matter is the Kinetic Theory of Gases, shadowed forth by Lucretius, definitely stated by Bernoulli, largely developed by Herapath, made a reality by Joule, and worked out in its present advanced state by Clausius and Maxwell. Joule, from the dynamical equivalent of heat, and his experiments upon the heat produced by the condensation of a gas, was able to estimate the average velocity of the ultimate molecules or atoms composing it…Clausius took fully into account the impacts of molecules on one another, and the kinetic energy of relative motions of the matter constituting an individual atom. He investigated the relation between their diameters, the number in a given space, and the mean length of path from impact to impact, and so gave formulation for estimates of the absolute dimensions of atoms…He explained the slowness of gaseous diffusion by the mutual impact of the atoms, and laid a secure foundation for a complete theory of the diffusion of fluids, previously a most refractory enigma. The deeply penetrating genius of Maxwell brought in viscosity and thermal conductivity, and thus completed the dynamical explanation of all known properties of gases, except their electrical resistance and brittleness to electric force. No such comprehensive molecular theory had ever been even imagined before the nineteenth century. Definite and complete in its area as it is, it is but a well-drawn part of a great chart, in which all physical science will be represented with every property known in dynamical relation to the whole. The prospect we now have of an early completion of this chart is based on the assumption of atoms. But there can be no permanent satisfaction on the minds in explaining heat, light, elasticity, diffusion, electricity, and magnetism in gases, liquids, and solids, and describing precisely the relations of these different states of matter to one another by statistics of great numbers of atoms, when the properties of the atom itself are simply assumed. When the work of the theory of which we have the first instalment in Clausius and Maxwell's work is complete, we are faced with a superlatively grand question, what is the inner mechanism of the atom?"[41].

### References

1  Brush S G, *Am J Phys*, 29 (1961) 593.
2  Hoyt C S, *J Chem Educ*, 24 (1947) 186.
3  Lucretius, *De Rerum Natura,* in *The Stoic and Epicurean Philosophers*: *The Complete Extant writing of Epicurus, Epictetus, Lucretius, Marcus Aurelius*, edited by Oates Whitney J (Random House, New York), 1940.
4  Hermann J, *Phoronomia, Sive de Viribus et Motibus Corporum Solidoum et Fluidorum Libri Duo* (Wetsten, Amsterdam), 1716.
5  Le Sage G L, *Nouveaux Mem Acad Roy Sci Belles-Lettres de Berlin,* (1784) 404.
6  Prevost P, *Traité de Physique Méchanique de George-Louis Le Sage Deux Traités de Physique Méchanique*, Geneva, 1818. The premier traité is Le Sage's "Physique Mecanique" and the second is Prevost´s "Quelques Nouvelles Applications des Principes Exposés dans le Premier Traité 1. Au Gaz, 2. À la Lumiére".
7  Bernstein H T, *Isis*, 54 Part 2(1963), 206.
8  Maxwell J C, *Encycl Brit*, 9th edn, Vol. 3, 1875, 36.
9  Thomson W, *Proc Roy Soc Edinburgh*, 7 (1872) 577; *Phil Mag*, 45 (1873) 321.
10 Dalton J, *A New System of Chemical Philosophy*, R. Bickerstaff, Manchester, 1808; in two volumes. Republished by Philosophical Library, New York, 1964; Part 1, section 2, pp 151.
11 Ampère A M, *Ann Chim*, 94 (1815) 145.
12 Ampère A M, *Bibliothèque, Universelle des Sciences, Belles-lettres et Arts,* (Genéve), 49 (1832) 225.

13  Ampère A M, *Ann Chim*, 58 (1835) 432.

14  Euler L, *Comm Acad Sci Petrop*, 2 (1719) 347.

15  Truesdell C, *Essays in the History of Mechanics* (Springer-Verlag, Berlin), 1968.

16  Bernoulli D, *Hydrodynamica, sive de viribus et motibus fluidorumcommentarii. Opus academicum ab auctore, dum Petropoli ageret, congestum*; J R Dulseckeri, 1738. Translated and reprinted as *Hydraulics* (Dover Publications, New York), 1968.

17  Amontons G, *Mém Acad Royale Sci,* (1702) 155.

18  Whitaker R D, *J Chem Educ*, 56 (1979) 325.

19  Herapath J, *Ann Phil*, 8 (1816) 56.

20  Brush S G, *Ann Sci*, 13 (1957) 188.

21  Brush S G, *Notes and Records Roy Soc*, 17 (1963) 161.

22  Brush S G, *Kinetic Theory,* Vol. I, The Nature of Gases and of Heat (Pergamon Press, Oxford), 1965.

23  Herapath J, *Ann Phil* [2], 1(1821) 273, 340, 401.

24  Wisniak J, *Indian J Chem Technol,* 11 (2004) 275.

25  Herapath J, *Mathematical Physics*, Whittaker & Co., London, 1847. Facsimile edition published by Johnson Reprint Corporation, London, 1972; (a) I, 242, (b) I, 249, (c) I, 267-269, (d) I, 278-279, (e) I, 343.

26  Brush S G, *Arch Hist Exact Sci*, 4 (1867) 145.

27  Wisniak J, *Indian J Chem Technol*, accepted (2005).

28  Waterston J J, *Proc Roy Soc*, 5 (1846) 604 (Abstract).

29  Haldane J S (*Editor*), *The Collected Papers of James Waterston* (Oliver and Boyd, Edinburgh-London), 1928.

30  Brush S G, *Ann Sci*, 13 (1957) 273.

31  Rankine W J M, *Trans Roy Soc, Edinburgh*, 20 (1853) 147.

32  Clausius R, *Ann Phys* [2], 100 (1857) 353; published in English in *Phil Mag*, 14 (1857) 108.

33  Krönig A K, *Poggendorf´s Annalender Physik*, 99 (1856) 315.

34  Brush S G, *Am Scientist*, 49 (1961) 202.

35  Clausius R, *Ann Phys*, 105 (1858) 239.

36  Clausius R, *Poggendorf´s Annalen*, 115 (1862) 1; published in English in *Phil Mag*, 23 (1862) 417.

37  Clausius R, (1879) 114. English translation in *Phil Mag*, 40 (1880) 122.

38  Joule J P, *Memoirs of the Manchester Literary and Philosophical Society*, 9 (1851) 107, November, 1851.

39  Maxwell J C, *Phil Trans*, 157 (1857) 49.

40  Jeans J H & Hille C E, *Encycl Brit*, 13 (1970) 352.

41  Thomson W, *Presidential Address*, 1871, British Association for the Advancement of Science, *Report*, xciii-xciv, London 1872.