# CHAPTER I

## INTRODUCTION

**1.** THE Kinetic Theory of Matter rests essentially upon two closely related hypotheses; the first—that of the molecular structure of matter, the second—the hypothesis that heat is a manifestation of molecular motion.

The first of these hypotheses belongs to the domain of chemistry; indeed it forms the basis of modern chemical science. It is believed not only that all matter is composed of a great number of molecules, but also that all molecules of the same chemical substance are exactly similar as regards size, mass, etc. If this were not so, it would be possible to separate the molecules of different types by chemical processes of fractionisation, whereas Dalton found that the successively separated fractions of a substance were exactly similar. It is true that very modern research has thrown some doubt on whether the molecules of a substance are all as exactly identical as they were once thought to be, but it is also true that the hypothesis of exact similarity of molecules is now, as a broad truth, unassailable, and forms a suitable and convenient working hypothesis for the Theory of Matter.

The second hypothesis, the identification of heat with molecular motion, is that with which the Kinetic Theory of Matter is especially concerned. This hypothesis was for long regarded as pure conjecture, incapable of direct proof, and probable just in proportion to the number of phenomena which could be explained by its help. In recent years, however, the study of the Brownian movements has provided brilliant visual demonstration of the truth of this conjecture, and the actual heat-motion of molecules—or at least of particles which play a rôle exactly similar to that of molecules—may now be seen by anyone who can use a microscope.

### The Three States of Matter.

**2.** One of the most striking and universal properties of the different kinds of matter is that of appearing in three distinct states—solid, liquid, and gaseous. Broadly speaking, the three states are associated with different

J. G.

1

ranges of temperature; as the temperature of a substance is raised, the sub-stance passes through the solid, liquid, and gaseous states in succession. It is natural to conjecture that the three states of matter are associated with three different types or intensities of molecular motion, and it is not difficult to see how the necessity for these three different states arises.

We know that two bodies cannot occupy the same space; any attempt to compel them to do so brings into play a system of repulsive forces tending to keep the two bodies apart, and this system of forces can only be interpreted as the aggregate of the forces from individual molecules. It follows that molecules exert forces on one another, and that these forces are, in general, repulsive when the molecules are sufficiently close to one another. On the other hand, the phenomenon of cohesion shews that the force between two molecules may, under certain conditions, be one of attraction.

**3.** *The solid state.* The fact that a solid body, when in its natural state, resists both compression and dilatation, indicates that the force between molecules changes from one of repulsion at small distances to one of attraction at greater distances. This change from a repulsive to an attractive force suggests a position of stable equilibrium in which a pair of molecules can rest in proximity to one another. If we imagine a great number of molecules placed in proximity and at rest in an equilibrium configuration, we have, on the Kinetic Theory conception of matter, a mass of matter in the solid state, and, as there is no motion, this matter must be supposed, in accordance with the fundamental hypothesis of the theory, to be entirely devoid of heat.

The molecules of which the substance is formed will be capable of vibration about their positions of equilibrium, and when these vibrations occur, we say that the body possesses *heat*. As the vibrations become more vigorous we say that the *temperature* of the body increases.

For example, we may imagine the vibratory motion of the molecules to be set up in the first instance by rubbing the surface of the body against a surface of a similar body: here we have a case of heat generated by friction. The act of rubbing will consist in first placing the surfaces of the two bodies so near to one another that the molecules near the surface of one exert a perceptible action on the molecules near the surface of the other, and then in moving the surfaces over one another so as to disturb these surface molecules from their positions of equilibrium. At first the motion will be confined to the neighbourhood of the parts actually rubbed, but the motion of these parts will gradually induce motion in the adjoining regions, until ultimately the motion will have spread over the whole mass.

As a second example, we may imagine two masses, both devoid of internal motion, to impinge one upon the other. The impact will at first cause systems of waves to be set up in the masses, but after a sufficient time the wave character of the motion will have become obliterated, whilst motion of some kind must persist in order to account for the energy of the original motion. This original motion will, in fact, have become replaced by a small vibratory motion of the molecules about their positions of equilibrium—according to the Kinetic Theory, by heat-motion.

**4.** *The liquid state.* If the body under consideration continues to acquire heat in any way—if, that is, the energy of vibration is caused continually to increase—a stage will in time be reached in which some of the molecules are possessed of so much kinetic energy that the forces from the other molecules no longer suffice to hold them in position: they will, to borrow an astronomical term, escape from their orbits. When the body has reached a state such that this is true of a great number of molecules, it is clear that the application of even a small force, provided it is continued for a sufficient length of time, will, by taking advantage time after time, as opportunity occurs, of the weakness of the forces tending to retain individual molecules, cause the mass to change its shape. When this stage is reached, the body has assumed a plastic or liquid state.

When a molecule of a liquid escapes from its orbit it will in general wander about amongst the other molecules until it falls into a new orbit. If, however, it was initially near to the surface of the liquid, it may be possible for it to escape altogether from the attraction of the other molecules, just as it is possible for a projectile, if projected from the earth's surface with sufficient velocity, to escape from the earth altogether. When this happens the molecule will leave the liquid, so that the mass and volume of liquid will continually diminish owing to the loss of such molecules. Here we have the Kinetic Theory interpretation of the process of evaporation, the vapour being formed by the escaped molecules.

If the liquid is contained in a closed vessel the escaping molecules will impinge on the side of the vessel, and after a certain number of impacts, may fall back again into the liquid. When a state is reached in which the number of molecules which fall back in this way is exactly balanced by the number which escape, we have, according to the Kinetic Theory, a liquid in equilibrium with its own vapour.

**5.** *The gaseous state.* If we suppose the whole of the liquid transformed into vapour in this way, we have the Kinetic Theory conception of a gas. The molecules can no longer be said to describe orbits, but describe rectilinear paths with uniform velocity except when they encounter other molecules or the walls of the containing vessel. It is clear that this view of the nature of a gas will sufficiently explain the property which a gas possesses of

spreading throughout the whole of any closed space in which it is placed. It is not necessary to suppose, as was at one time done, that this expansive property of a gas is the result of repulsive forces between the molecules.

The fundamental accuracy of this conception of the gaseous state is finely illustrated by some experiments of Dunoyer*. A cylindrical tube was divided into three compartments by means of two partitions perpendicular to the axis of the tube, and these partitions were then pierced in their centres by small holes, so as to form diaphragms. The tube was fixed vertically and in its lowest compartment was placed a piece of some substance, such as sodium, which is in the solid state at ordinary temperatures. After exhausting the tube of all air, the sodium (or other substance) was heated to a sufficient temperature to vaporise it. As the molecules of the vapour are shot off, they move in various directions, and the majority strike on the walls of the lowest compartment of the tube and form a deposit there. Some however pass through the first diaphragm, and describe paths radiating out from the hole in this diaphragm. A few of the molecules pass through both diaphragms into the upper compartment of the tube. These do not collide, for their paths cannot intersect since they are rectilinear paths all radiating from the same point, namely the hole in the lower diaphragm. They accordingly form a deposit on the top of the tube, and this deposit is found to coincide exactly with the projection of the hole in the second diaphragm formed by radii drawn from the hole in the first diaphragm. If a small obstacle is placed in the path of these molecules, it will be found to form a "shadow" on the upper surface of the tube; it may even be that an umbra and penumbra will be discernible.

### *Mechanical Illustration of the Kinetic Theory of Gases.*

6. The Kinetic Theory of Matter is best approached through a study of the Kinetic Theory of the gaseous state. Indeed, until very recently, the Kinetic Theory of Matter has been identical with the Kinetic Theory of Gases; there has not been sufficient evidence as to the conditions prevailing in the solid and liquid states to formulate a Kinetic Theory of these states. The requisite evidence is now rapidly accumulating, so that theories of the solid and liquid states are becoming possible, in outline at least, but it is still true that the theory of gases is much more developed and complete than the corresponding theories of liquids and solids can possibly be, and the earlier chapters of the present book are devoted especially to the consideration of the gaseous state.

7. It is important to form as clear an idea as possible of the conception of the gaseous state on which the Kinetic Theory is based, and this can best be done by considering a mechanical illustration.

* L. Dunoyer, *Comptes Rendus*, 152 (1911), p. 592, and *Le Radium*, VIII. (1911), p. 142.

Very little is known as to the structure or shape of actual molecules, or the way in which they react upon one another. Since, however, it is desirable to have as concrete a representation as possible before the mind, at least at the outset, we may (following a procedure which is very usual in the development of the Kinetic Theory) agree for the present to associate the idea of a molecule with that of a spherical body of great elasticity and rigidity—to make the picture quite definite, let us say a billiard-ball. The justification for this procedure lies in its success: it will be found that the behaviour of a gas in which the molecules are complex structures of the most general kind can, to a large extent, be predicted from the behaviour of a much simpler imaginary gas in which the molecules are of the type just described. In fact, one of the most striking features of the Kinetic Theory is the extent to which it is possible to predict the behaviour of a gas as a whole, while remaining in almost complete ignorance of the behaviour and properties of the molecules of which it is composed. Indeed, so many of the results of the theory are true for all kinds of molecules that they would remain true even if the molecules actually were billiard-balls.

As it is somewhat difficult to imagine in detail the motion of a large number of spheres flying about in three dimensions, we may conveniently confine ourselves to a consideration of the analogous motion in two dimensions. As the molecules of the gas are to be represented by billiard-balls, let us suppose the vessel in which the gas is enclosed to be represented by a large billiard-table. The walls of the vessel will of course be represented by the cushions of the table, and if the vessel to be represented is a closed one, the table must have no pockets. Finally, the materials of the table must be supposed of such ideal quality that a ball once set in motion will collide many thousands of times with the cushions before being brought to rest by the friction and the various other passive forces which tend to destroy its motion. A great number of the properties of gases can be illustrated with this imaginary apparatus.

If we take a very large number of balls, and start them at random on the table with random velocities, the resulting state of motion will give a representation of what is supposed to be the condition of matter in its gaseous state. Every ball will be continually colliding both with the other balls and with the cushions of the table. The velocities of the balls will be of the most varying kinds: at one instant a ball may be brought absolutely to rest, while at another instant, as the result of a succession of favourable collisions, it may possess a velocity far in excess of the average velocity of the other balls. One of the problems we shall have to solve will be to find how the velocities of the various balls are distributed about the mean velocity. We shall find that whatever the way in which the velocities are grouped at the outset, they will tend, after a sufficient number of collisions, to group

themselves according to the so-called law of trial and error—the law which governs the grouping in position of shots fired at a target.

If the cushions of the table were not fixed in position, they would be driven back by the continued impacts of the balls. The force exerted on the cushions by the balls colliding with them accordingly represents the pressure exerted on the walls of the containing vessel by the gas. Let us imagine a moveable barrier placed initially against one of the cushions, and capable of motion parallel to this cushion. Moving this barrier forward is equivalent to decreasing the volume of the gas. If the barrier is moved forwards while the motion of the billiard-balls is in progress, the impacts both on the moveable barrier and on the three fixed cushions will of course become more frequent : here we have a representation of an increase of pressure accompanying a diminution of volume of a gas. We shall have to discuss how far the law connecting the pressure and density of a gas, constituted in the way imagined by the Kinetic Theory, is in agreement with that found by experiment for an actual gas.

Let us imagine the barrier on our supposed billiard-table to be moved half-way up the table. Let us suppose that the part of the table in front of the barrier is occupied by white balls moving on the average with a large velocity, while the part behind it is similarly occupied by red balls moving on the average with a much smaller velocity. Here we may imagine that we have divided our vessel into two separate chambers; the one is occupied by a gas of one kind at a high temperature, the other by a gas of a different kind at a lower temperature. Returning to the billiard-table, let the barrier suddenly be removed. The white balls will immediately invade the part which was formerly occupied only by red balls, and vice versa. Also the rapidly moving white balls will be continually losing energy by collision with the slower red balls, and the red of course gaining energy through impact with the white. After the motion has been in progress for a sufficient time the white and red balls will be equally distributed over the whole of the table, and the average velocities of the balls of the two colours will be the same. Here we have simple illustrations of the diffusion of gases, and of equalisation of temperature. The actual problem to be solved is, however, obviously more complex than that suggested by this analogy, for in nature the molecules of different gases differ by something more fundamental than mere colour.

One further question must be considered. No matter how elastic the billiard-balls and table may be, the motion cannot continue indefinitely. In time, the energy of this motion will be frittered away, partly perhaps by frictional forces, such as air-resistance, and partly by the vibrations set up in the balls by collisions. The energy dissipated by air-resistance becomes transformed into energy in the air; the energy dissipated by collisions is

transformed into energy of internal vibrations of the billiard-balls. What, then, does this represent in the gas, and how is it that a gas, if constituted as we have supposed, does not, in a very short time, lose the energy of translational motion of its molecules, and replace it by energy of internal vibrations of these molecules, and energy in the surrounding ether?

The difficulties raised by this and similar questions formed a most serious hindrance to the progress of the Kinetic Theory for many years. Attention was drawn to them by Maxwell, but it was not until the introduction of the Quantum-theory by Planck and his followers in the early years of the present century, that it was possible to give anything like a satisfactory explanation. The explanation supplied by the Quantum-theory will have to be examined in detail in a later chapter of the present book. It is at best only partial, but must, so far as it goes, probably be regarded as satisfactory. The explanation is, in brief, that there is no true analogy between the two cases when we consider questions of internal vibrations and transfer of energy to the surrounding medium. For the motion of the billiard-balls is governed by the well-known Newtonian laws, whereas the internal motions of molecules, and their transfer of energy to the ether, are now believed to be governed by an entirely different system of dynamical laws. The procedure of this book will be to develop the Kinetic Theory as far as it can be developed without departure from the Newtonian laws, and then to examine what light can be thrown on the various outstanding phenomena by the new system of dynamical laws suggested by Planck.

### Numerical Values.

**8.** The foregoing rough sketch will, it is hoped, have given some idea of the nature of the problems to be attacked. As a conclusion to this preliminary chapter, it may be useful to give some approximate numerical values. These will give an indication of the order of magnitude of the quantities with which we shall be dealing, and will make it easier to form a clear mental picture of the processes under consideration.

*Number of molecules per cubic centimetre.* In accordance with the law of Avogadro (see below, § 147), the number of molecules in a cubic centimetre of gas at standard temperature and pressure (0° C. and 1 atmosphere) is independent of the chemical composition of the gas. This number, which will be denoted by $N_0$, is frequently referred to as Avogadro's number, and its numerical evaluation is naturally of great importance for the Kinetic Theory of Matter. Unfortunately the number is extremely difficult to evaluate with any great accuracy: many of the uncertainties in the numerical values used in the Kinetic Theory may be referred ultimately to uncertainties in the estimation of this number. It is fortunate that there are a great

number of methods available for the determination of $N_0$.

The best determination of $N_0$ is that deduced from the value of the charge on the electron. Millikan* determines this, with a probable error of about one part in a thousand, as

$$e = 4\cdot774 \times 10^{-10} \text{ electrostatic units}$$

$$= 1\cdot592 \times 10^{-20} \text{ electromagnetic units.}$$

Since $N_0 e$ is the constant of electrolysis, and therefore equal to $9649\cdot6$ electromagnetic units, the corresponding value of $N_0$ is

$$N_0 = 2\cdot705 \times 10^{19}.$$

The density of hydrogen (molecular weight $2\cdot016$) at standard temperature and pressure is $\cdot00008987$, so that, if $N_1$ is the number of molecules in one gram-molecule, we have

$$N_0 = \cdot00004458 \, N_1.$$

Thus the above value of $N_0$ corresponds to

$$N_1 = 6\cdot062 \times 10^{23}.$$

A less accurate determination of $N_0$ is obtained from a study of black-body radiation. Richardson† obtains the value $N_0 = 2\cdot76 \times 10^{19}$, but a recalculation in which use is made of more recent observational data, shews that the value of $N_0$ must be very close to the value $N_0 = 2\cdot705 \times 10^{19}$ given above.

Another determination of $N_1$ can be made from observations on the Brownian Movements. The method was first developed by Perrin, who obtained values uniformly larger than Millikan's value given above. More recent observations by H. Fletcher‡ give the value $N_1 = 6\cdot03 \times 10^{23}$, with a probable error of about 2 per cent. of the whole.

For the purpose of calculations in the present book we shall adopt Millikan's values

$$N_0 = 2\cdot705 \times 10^{19},$$

$$N_1 = 6\cdot062 \times 10^{23}, \text{ the number of molecules in 1 gm.-mol.,}$$

$$e = 4\cdot774 \times 10^{-10} \text{ electrostatic units.}$$

Thus at $0°$ C. and at a pressure of 1 atmosphere (760 mm.), there are taken to be $2\cdot705 \times 10^{19}$ molecules per cubic centimetre. Under other conditions the number is of course directly proportional to the density.

The average distance apart of adjacent molecules at atmospheric pressure will clearly be about $(2\cdot705 \times 10^{19})^{-\frac{1}{3}}$ cms., or $3\cdot33 \times 10^{-7}$ cms. At a pressure of one-millionth of an atmosphere ($\cdot00076$ mm.) this distance is increased to $3\cdot33 \times 10^{-5}$ cms. ($\cdot00033$ mm.).

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* *Phil. Mag.* xxxiv. (1917), p. 1.        † *Electron Theory of Matter*, p. 356.
‡ *Phys. Rev.* iv. (1914), p. 440.

*Mass of a molecule.*   Since we are taking $N_1 = 6 \cdot 062 \times 10^{23}$, the mass of the atom of unit atomic weight must be taken to be $(6 \cdot 062 \times 10^{23})^{-1}$ gms. or $1 \cdot 651 \times 10^{-24}$ gms.   Thus the hydrogen atom, of atomic weight $1 \cdot 008$, will be of mass $1 \cdot 662 \times 10^{-24}$ gms., and the masses of molecules will be in proportion to their molecular weights; that of oxygen for instance is $52 \times 10^{-24}$ gms.

*Velocity.*   The velocity of the molecules does not depend on the evaluation of Avogadro's number, and is known with great accuracy (see below, §150).

For air at a temperature of 15° C. the average velocity is about 459 metres per second.   For hydrogen at 0° C. it is about 1694 metres per second.   As regards velocities under other conditions it may be said that, roughly, the mean velocity of a molecule of molecular weight $m$, at a temperature of $\theta$ degrees Centigrade, is proportional to $\sqrt{273 + \theta}$, and is inversely proportional to $\sqrt{m}$, so that, for instance, the velocity of the oxygen molecule is approximately a quarter of that of the hydrogen molecule at the same temperature.   The velocity is independent of the density of the gas.   A table of velocities will be given later (§151).

Since the molecules of hydrogen at 0° C. move with an average velocity of 1694 metres a second, the total distance described by the $2 \cdot 705 \times 10^{19}$ molecules in a c.c. of hydrogen at 0° C. will be $458 \times 10^{17}$ kilometres per second.

*Size.*   It is a matter of some difficulty to determine or even to define the size of a molecule.   The trouble arises primarily from our ignorance of the shape and other properties of the molecule.   If the molecules were known to be elastic spheres the question would be simple enough, and the size of the molecule would be measured by the diameter of the sphere.   If, however, the molecules are *assumed* as a first approximation to be elastic spheres, experiment leads to discordant results for the diameters of these spheres, shewing that the original assumption is unjustifiable.   The divergences arise not only from the fact that the shape of the molecules is not spherical, but also from the fact that the molecules are surrounded by fields of force, and in most experiments it is the extension of this field of force, rather than that of the molecules themselves, with which we are concerned.

If, however, we agree to regard the molecules as roughly represented by elastic spheres, it is found that these spheres must be supposed in the case of hydrogen to have a radius of about $1 \cdot 36 \times 10^{-8}$ cms.   The size ought strictly to be different for different molecules, and more exact figures will be given later, but as the difference in size is hardly more than comparable with the error introduced by the supposition that the molecules are elastic spheres, these differences need not be discussed here.   A full discussion of the evidence of the Kinetic Theory as to the size of molecules will be found in Chapter XIV of the present book.

*Number and frequency of collisions.* Regarding the molecule of hydrogen as a sphere of radius $1\cdot36 \times 10^{-8}$ cms. the number of collisions per cubic centimetre of hydrogen at $0°$ C. is found to be about $2\cdot037 \times 10^{29}$ per second.

*Free paths.* Each collision is the termination of two free paths, hence the number of free paths described in the gas just considered is about $4\cdot07 \times 10^{29}$ per second. It has already been said that the total distance described—*i.e.* the aggregate of these free paths—is $458 \times 10^{22}$ cms. Hence on division we see that the mean length of these free paths is $1\cdot125 \times 10^{-5}$ cms.

It is obvious that the mean free path, being a pure length, will depend only on the diameter of the molecules, and on the number of molecules per cubic centimetre; it will not depend on the velocities of motion of the molecules. Thus the values we have obtained for the mean free path are approximately true for all gases so long as the molecules are supposed uniformly to be spheres of radius $1\cdot36 \times 10^{-8}$ cms. The free path is, however, inversely proportional to the number of molecules per cubic centimetre of gas. For instance in a vacuum tube in which the pressure is that of half a millimetre of mercury, the density of gas is only $1:1520$ of the normal density, and therefore the free path is roughly equal to one-sixth of a millimetre.

It appears from these figures that the mean free path of a molecule is about 400 times its diameter in a gas at normal pressure, and is about 600,000 times its diameter when the pressure is reduced to half a millimetre of mercury. There is therefore every justification for assuming, as a first approximation, that the linear dimensions of molecules are small in comparison with their free paths.

Comparing the values obtained for the length of the free path with the values previously given for the velocity of motion, we find that the mean time of describing a free path ranges from about $3 \times 10^{-10}$ seconds in the case of air under normal conditions, to about $10^{-7}$ seconds in the case of hydrogen at $0°$ C. at a pressure equal to that of half a millimetre of mercury.

The principal lesson to be learned from the foregoing figures is that the mechanism of the Kinetic Theory is extremely "fine-grained" when measured by ordinary standards. Molecules are, in fact, not infinitely small, and neither is their motion infinitely rapid, but the units of space and time appropriate for the measurement of the motion of individual molecules are so small in comparison with even the smallest quantities which we can measure experimentally that the phenomena exhibited by a gas constituted in the way described will be indistinguishable, so far as experiment and human observation go, from those of a continuous medium.