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Chapter I

INTRODUCTION

The Origins of the Theory

1. As soon as man began to think of abstract problems at all, it was only natural that speculations as to the nature and ultimate structure of the material world should figure largely in his writings and philosophies.

Among the earliest speculations which have survived are those of Thales of Miletus (about 640–547 B.C.), many of whose ideas may well have been derived from still earlier legends of Egyptian origin. He conjectured that the whole material universe consisted only of water and of substances derived from water by physical transformation. Earth was produced by the condensation of water, and air by its rarefaction, while air when heated became fire. About 500 B.C. Heraclitus advanced the alternative view that earth, air, fire and water were not transformable one into the other, but constituted four distinct unalterable "elements", and that all material substances were composed of these four elements mixed in varying proportions—a sort of dim anticipation of modern chemical theory. At a somewhat later date, Leucippus and Democritus maintained that matter consisted of minute hard particles moving as separate units in empty space, and that there were as many kinds of particles as there are different substances.

Unhappily nothing now remains of the writings of either Democritus or Leucippus; their opinions are known to us only through second-hand accounts. From these we learn that they imagined their particles to be eternal and invisible, and so small that their size could not be diminished; hence the name ἄτομος—indivisible. The particles of any particular substance, such as iron or water, were supposed to be all similar to one another, and every one of them carried in itself all the attributes of the substance. For instance, Democritus taught that the atoms of water, being smooth and round, are unable to hook on to each other, so that they roll over and over like small globes; on the other hand, the atoms of iron, being rough, jagged and uneven, cling together to form a solid body. The "atoms" of the Greeks corresponded of course to the molecules of modern chemistry.

Similar views were advocated by Epicurus (341–276 B.C.), but rejected by Aristotle. In a later age (A.D. 55) Lucretius advanced substantially identical ideas in his great poem *De rerum natura*. In this he claimed only to expound the views of Epicurus, most of whose writings are now lost.

Lucretius explains very clearly that the atoms of all bodies are in ceaseless motion, colliding and rebounding from one another. When the distances which the atoms cover between successive rebounds are small, the substance is in the solid state; when large, we have "thin air and bright sunshine". He further explains that atoms must be very small, as can be seen either from the imperceptible wearing away of objects, or from the way in which our clothes can become damp without exhibiting visible drops of moisture.*

There was little further discussion of the problem until the middle of the seventeenth century, when Gassendi† examined some of the physical consequences of the atomic view. He assumed his atoms to be similar in substance, although different in size and form, to move in all directions through empty space, and to be devoid of all qualities except absolute rigidity. With these simple assumptions, Gassendi was able to explain a number of physical phenomena, including the three states of matter and the transitions from one to another, in a way which differed but little from that of the modern kinetic theory. He further saw that in an ordinary gas, such as atmospheric air, the particles must be very widely spaced, and he was, so far as we know, the first to conjecture that the motion of these particles could account by itself for a number of well-known physical phenomena, without the addition of separate *ad hoc* hypotheses. All this gives him a very special claim to be regarded as the father of the kinetic theory.

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* See an essay by E. N. da C. Andrade, "The Scientific Significance of Lucretius", Munro's *Lucretius*, 4th edition (Bell, 1928).

† *Syntagma Philosophicum*, 1658, Lugduni.

Twenty years after Gassendi, Hooke advanced somewhat similar ideas. He suggested that the elasticity of a gas resulted from the impact of hard independent particles on the substance which enclosed it, and even tried to explain Boyle's law on this basis.

Newton accepted these views as to the atomic structure of matter, although he suggested a different explanation of Boyle's law*. He wrote†

"It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles ..., and that these primary particles, being solids, are incomparably harder than any porous bodies compounded of them; even so hard as never to wear or break in pieces."

Hooke was followed by Daniel Bernoulli,‡ who is often credited with many of the discoveries of Gassendi and Hooke. Bernoulli, again supposing that gas-pressure results from the impacts of particles on the boundary, was able to deduce Boyle's law for the relation between pressure and volume. In this investigation the particles were supposed to be infinitesimal in size, but Bernoulli further attempted to find a general relation between pressure and volume when the particles were of finite size, although still absolutely hard and spherical.

After Bernoulli, there is little to record for almost a century. Then we find Herapath§ (1821), Waterston|| (1845), Joule¶ (1848), Kronig** (1856), Clausius (1857) and Maxwell (1859) taking up the subject in rapid succession.

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* See § 50, below.

† *Opticks*, Query 31 (this did not appear until the second edition of the *Opticks*, 1718).

‡ Daniel Bernoulli, *Hydrodynamica*, Argentoria, 1738: Sectio decima, "De affectionibus atque motibus fluidorum elasticorum, praecipue autem aeris."

§ *Annals of Philosophy* (2), **1**, p. 273.

|| *Phil. Trans. Roy. Soc.* **183** (1892), p. 1. Waterston presented a long paper to the Royal Society in 1845, but this contained many inaccuracies and so was not published until Lord Rayleigh secured its publication, for what was then a purely historical interest, in 1892.

¶ *British Association Report*, 1848, Part II, p. 21; *Memoirs of the Manchester Literary and Philosophical Society* (2), **9**, p. 107.

** *Poggendorff's Annalen.*

In his first paper* Clausius calculated accurately the relation between the temperature, pressure and volume in a gas with molecules of infinitesimal size; he also calculated the ratio of the two specific heats of a gas in which the molecules had no energy except that of their motion through space. In 1859, Clerk Maxwell read a paper before the British Association at Aberdeen,† in which the famous Maxwellian law of distribution of velocities made its first appearance, although the proof by which Maxwell attempted to establish it is now universally agreed to have been invalid.‡ In the hands of Clausius and Maxwell the theory developed with great rapidity, so that to write its history from this time on would be hardly less than to give an account of the subject in its present form.

The Three States of Matter

2. Most substances are capable of existing in three distinct states, which we describe as solid, liquid and gaseous. The typical example is water, with its three states of ice, water and steam. It is natural to conjecture that the three states of matter correspond to three different types or intensities of motion of the fundamental particles of which the matter is composed, and it is not difficult to see how the necessity for these three different states may arise.

We know that two bodies cannot occupy the same space; if we try to make them do so, repulsive forces come into play, and keep the two bodies apart. If matter consists of innumerable particles, these forces must be the aggregate of the forces from individual particles. These particles can, then, exert forces on one another, and the forces are repulsive when the particles are pushed sufficiently close to one another. If we try to tear a solid body into pieces, another set of forces comes into play—the forces of cohesion. These also indicate the existence of forces between individual particles, but the force between two particles is no longer one of repulsion; it is now one of attraction. The fact that a solid body, when in its natural state, resists both compression

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* "Ueber die Art der Bewegung welche wir Wärme nennen", *Pogg. Ann.* **100**, p. 353.

† *Phil. Mag.* Jan. and July 1860; *Collected Works*, **1**, p. 377.

‡ See Appendix I, p. 296.

and dilatation, shews that the force between particles changes from one of repulsion at small distances to one of attraction at greater distances, as was pointed out by Boscovitch in 1763.*

3. *The Solid State.* Somewhere between these two positions there must be a position of stable equilibrium in which two particles can rest in proximity without either attracting or repelling one another. If we imagine a great number of particles placed in such proximity, and so at rest in their positions of equilibrium, we have the kinetic theory conception of a mass of matter in the solid state—a solid body. Modern X-ray technique makes it possible to study both the nature and arrangement of these particles. In solid bodies of crystalline structure, the "particles" are atoms and electrons, arranged in a regular three-dimensional pattern;† in conductors the electrons are free to thread their way between the atoms.

When the particles which constitute a solid body oscillate about their various positions of equilibrium, we say that the body possesses heat. The energy of these oscillatory motions is, in fact, the heat-energy of the body. As the oscillations become more vigorous, we say that the temperature of the body increases.

We may make a definite picture by supposing that the oscillatory motions are first set up by rubbing two solid objects together. We place the surfaces of the two bodies so close to one another that the particles near the surface of one exert perceptible forces on the particles near the surface of the other; we then move the surfaces over one another, so that the forces just mentioned draw or push the surface particles from their positions of equilibrium. At first, the only particles to be disturbed will be those which are in the immediate neighbourhood of the parts actually rubbed, but gradually the motion of these parts will induce motion in the adjoining regions, until ultimately the motion spreads over the whole mass. This motion represents heat which was, in the first instance, generated by friction, and then spread by conduction through the whole mass.

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* Theoria Philosophiae Naturalis (Venice, 1763; English translation, Open Court, Chicago and London, 1922). See especially §§ 74 ff.

† See W. L. Bragg, *Crystal Structure*, and innumerable other books and papers.

As a second example, we may imagine that two solid bodies, both devoid of internal motion, impinge one upon the other—as for instance a hammer upon a clock-bell. The first effect of this impact will be that trains of waves are set up in the two bodies, but after a sufficient time the wave character of the motion will become obliterated. Motion of some kind must, however, persist in order to account for the energy of the original motion. This original motion will, in actual fact, be replaced by small vibratory motions in which the particles oscillate about their positions of equilibrium—according to the kinetic theory, by heat motion. In this way the kinetic energy of the original motion of the solid bodies is transformed into heat-energy.

4. *The Liquid State.* If a solid body acquires more heat, the energy of its vibrations will increase, so that the excursions of its particles from their positions of equilibrium will become larger. If the body goes on acquiring more and more heat, some of the particles will ultimately be endowed with so much kinetic energy that the forces from the other particles will no longer be able to hold them in position; they will then, to borrow an astronomical term, escape from their orbits, and move to other positions. When a considerable number of particles are doing this, the application of even a small force, provided it is continued for a sufficient length of time, can cause the mass to change its shape; it does this by taking advantage time after time, as opportunity occurs, of the weakness of the forces tending to retain individual particles.

If still more heat is provided, a greater and greater number of the particles will move freely about; finally, when all the particles are all doing this, the body has attained the state we describe as liquid.

So long as the body is in the solid state, the particles which execute vibrations will usually be either isolated electrons or atoms. In the liquid state it is comparatively rare for either electrons or atoms to move as independent particles, because the forces binding these into molecules are usually too strong to be overcome by the heat-motion; thus the particles which move independently in a liquid are generally complete molecules.

Until recently it was supposed that the molecules of a liquid moved at random, and shewed a complete disorder in their arrangement—in sharp contrast to the orderly arrangement of the particles in a solid. Recent investigations suggest the need for modifying this view. A molecule in a liquid is probably acted on all the time by about as many other molecules as it would be if in the solid state. The forces from these neighbouring molecules imprison it in a cell from which it only rarely escapes. The main difference between a solid and a liquid is not that between captivity and freedom; it is only that the particle of a solid is held in fetters *all* the time, while that of a liquid is held in fetters *nearly all* the time, living a life of comparative freedom only in the very brief intervals between one term of imprisonment and the next. Further X-ray technique has shewn that there is a certain degree of regularity and order in the arrangement of the liquid molecules in space.*

This knowledge is derived only from a statistical study of the molecules of a liquid; no known technique makes it possible to see the wanderings of individual molecules. Perhaps this is not surprising, since even the largest of molecules are beyond the limits of vision in the most powerful of microscopes. But if a number of very small solid particles—as, for instance, of gamboge or lycopodium—are placed in suspension in a liquid, these particles are set into motion as the moving molecules of the liquid collide with them and hit them about, now in this direction and now in that. These latter motions can be seen through a microscope, so that the solid particles act as indicators of the motions of the molecules of the liquid, and so give a very convincing, even if indirect, proof of the truth of the kinetic theory conception of the liquid state. They are called Brownian movements, after the English botanist, Robert Brown.

For, in 1828 Brown had suspended grains of pollen in water, and examined the mixture through a microscope. He found that the pollen grains were engaged in an agitated dance, which was to all appearances continuous and interminable. His first thought was that he had found evidence of some vital property in the pollen,

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* See in particular, "Recent Theories of the Liquid State", N. F. Mott and R. W. Gurney, *Physical Society Reports on Progress in Physics* (C.U. Press), 5 (1939), p. 46.

but he soon found that any small particles, no matter how non-vital, executed similar dances. The true explanation, that the particles were acting merely as indicators of the molecular motion of the liquid in which they were immersed, was given by Delsaux in 1877 and again by Gouy in 1888. A full mathematical theory of the movements was developed by Einstein and von Smoluchowski about 1905.*

In 1909 Perrin suspended particles of gamboge in a liquid of slightly lower density, and found that the heavy particles did not sink to the bottom of the lighter liquid; they were prevented from doing so by their own Brownian movements. If the liquid had been infinitely fine-grained, with molecules of infinitesimal size and weight, every solid particle would have had as many impacts from above as below; these impacts, coming in a continuous stream, would have just cancelled one another out, so that each particle would have been free to fall to the bottom under its own weight. But when they were bombarded by molecules of finite size and weight, the solid particles were hit, now in one direction and now in another, and so could not lie inertly on the bottom of the vessel. From the extent to which they failed to do this, Perrin was able to form an estimate of the weights of the molecules of the liquid (§ 16, below) and this agreed so well with other estimates that there could be but little doubt felt as to the truth either of the kinetic theory of liquids, or of the associated explanation of the Brownian movements.

A molecule of a liquid which has escaped from its orbit in the way described on p. 6 may happen to come near to the surface of the liquid, in which case it may escape altogether from the attraction of the other molecules, just as a projectile which is projected from the earth's surface with sufficient velocity may escape from the earth altogether. When this happens the molecule leaves the liquid, and the liquid must continually diminish both in mass and volume owing to the loss of such molecules, just as the earth's atmosphere continually diminishes owing to the escape of rapidly moving molecules from its outer surface. Here we have the kinetic theory interpretation of the process of evaporation, the vapour being, of course, formed by the escaped molecules.

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* See § 180, below.

If the liquid is contained in a closed vessel, each escaping molecule must in time strike the side or top of the vessel; its path is now diverted, and it may fall back again into the liquid after a certain number of impacts. In time a state may be reached such that as many molecules fall back in this way as escape by evaporation; we now have, according to the kinetic theory, a liquid in equilibrium with its own vapour.

5. *The Gaseous State.* On the other hand, it is possible for the whole of the liquid to be transformed into vapour in this way, before a steady state is reached. Here we have the kinetic theory picture of a gas—a crowd of molecules, each moving on its own independent path, entirely uncontrolled by forces from the other molecules, although its path may be abruptly altered as regards both speed and direction, whenever it collides with another molecule or strikes the boundary of the containing vessel. The molecules move so swiftly that even gravity has practically no controlling effect on their motions. An average molecule of ordinary air moves at about 500 metres a second, so that the parabola which it describes under gravity has a radius of curvature of about 25 kilometres at its vertex, and even more elsewhere. This is so large in comparison with the dimensions of any containing vessel that we may, without appreciable error, think of the molecules as moving in straight lines at uniform speeds, except when they encounter either other molecules or the walls of the containing vessel. This view of the nature of a gas explains why a gas spreads immediately throughout any empty space in which it is placed; there is no need to suppose, as was at one time done, that this expansive property is evidence of repulsive forces between the molecules (cf. § 50, below).

As with a liquid, so with a gas, there is no absolutely direct evidence of the motions of individual molecules, but an indirect proof, at one remove only, is again provided by the Brownian movements. For these occur in gases as well as in liquids; minute particles of smoke* and even tiny drops of oil floating in a gas may be seen to be hit about by the impact of the molecules of the gas.

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* Andrade and Parker, *Proc. Roy. Soc.* A, **159** (1937), p. 507.

Recently E. Kappler* constructed a highly sensitive torsion-balance, in which the swinging arm was free to oscillate in an almost perfect vacuum. The swinging arm had a moment of momentum of 0·235 millionth of a gm. cm.^{2}, and when it swung in a gas at pressure of only a few hundreds of a millimetre of mercury, its period of oscillation was about 15 seconds. When the oscillations were recorded on a moving photographic film, it was seen that they did not proceed with perfect regularity. The speed of motion of the arm experienced abrupt changes, and, as we shall see later (p. 129), there can be no doubt that these were caused by the impacts of single molecules of the gas.

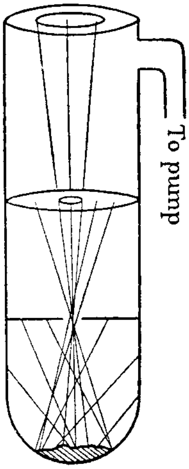

Fig. 1

Perhaps, however, the simplest evidence of the fundamental accuracy of the kinetic theory conception of the gaseous state is to be found in experiments of a type first performed by Dunoyer.† He divided a cylindrical tube into three compartments by means of two partitions perpendicular to the axis of the tube, these partitions being pierced in their centres by small holes, as in fig. 1. The tube was fixed vertically, and all the air pumped out. A small piece of sodium was then introduced into the lowest compartment, and heated to a sufficient temperature to vaporise it. Molecules of sodium are now shot off, and move in all directions. Most of them strike the walls of the lowest compartment of the tube and form a deposit there, but a few escape through the hole in the first partition, and travel through the second compartment of the tube. These molecules do not collide with one another, since their paths all radiate from a point—the small hole through which they have entered the compartment; they travel like rays of light issuing from a source at this point. Some travel into the uppermost compartment through the opening in the second partition, and when they strike the top of the tube, make a deposit there.

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* *Ann. d. Phys.* **31** (1938), p. 377.

† L. Dunoyer, *Comptes Rendus*, **152** (1911), p. 592, and *Le Radium*, **8** (1911), p. 142.