

THE KINETIC THEORY OF GASES

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TRANSLATOR'S NOTE

THIS translation is taken from Professor Bloch's work, dated 1921. The original text has, I hope, been faithfully reproduced with a few minor exceptions. In one or two cases, particularly in the sections dealing with statistical mechanics and probability, the mathematical presentation has been slightly modified where I deemed it advisable in the interest of clearness, but the method has not been changed in any way. Here and there changes have been made in the numerical data in the light of more recent work. At the request of the publishers of this translation I have prepared a more complete bibliography of the subject, which appears at the end of the book, including a list of the more important original papers concerning subjects which commonly find no place in the average text-book. It is hoped the references included will serve as a "point d'appui" for further study.

P. A. S.

NORTON HALL
NORTON-ON-TEES

PREFACE

DISCONTINUOUS STRUCTURE OF MATTER

FUNDAMENTAL HYPOTHESES

THE kinetic theory of gases is merely a branch—albeit the most perfect and most completely developed branch—of the molecular theory of matter. It states that the continuity of matter, solid, liquid, or gaseous, is only apparent, hiding a real discontinuity beyond the limits of our perception. Matter, in all its states, is an agglomeration of very small, distinct particles, whose mutual interactions and movements depend on temperature and pressure, forming an assembly which resembles a continuous medium. In solids the particles oscillate comparatively feebly about their mean positions of equilibrium. In liquids their movements are less restricted and give place to free gliding motions of the particles relative to one another: their mutual interaction still preserves a cohesion of the whole and consequently an approximately constant volume, but its shape no

longer remains invariable as in the case of solids. Finally, in gases, the particles escape almost completely from their mutual interactions, cohesion becomes very weak or negligible, and henceforth the movements which animate the particles become practically rectilinear and are only disturbed by incessant collisions with other particles or with the wall of the containing vessel. These latter collisions are the origin of the pressure which the gas exerts on the wall; the freedom of molecular motions, on the other hand, explains the diffusion of the gas into every space open to it or into another gas.

The theory of gases is more easily developed than that of the other states of matter; the almost complete absence of cohesive forces, the unknown law of which plays an essential role in the condensed states, and the relatively disperse condition of the molecules, which may, as a first approximation, be considered as material points, introduce great simplifications in our reasoning and calculation. These we shall consider at some length, only discussing the theory of liquids and solids as a subsidiary study.

From the physical point of view, the essential feature of the theory is that heat is no longer considered as a variety of energy distinct from mechanical energy. It is the molecular agitation, or more precisely, the kinetic energy of the molecules, which represents the major part of the heat contained in the gas.

The surplus is accounted for by the potential energy of intermolecular attractions. We see then that the principle of the equivalence of heat and work is, in a sense, visualised from the start by the very conception we hold of heat itself. Hence the name "mechanical theory of gases" which is sometimes given to this doctrine.

On the other hand, since direct experiment does not permit us to distinguish the molecules and their individual movements, the observable properties of gases can only be mean properties, attributable, that is to say, to the simultaneous and more or less similar actions of an immense number of molecules. The physical aim of the theory is to deduce these mean properties from complicated and apparently inextricable molecular motions.

The mathematical calculations to which we are led should, therefore, bear upon these motions, the details of which are unknown to us and whose general characters alone we are able to imagine. They should lead to average results which will depend upon these general characteristics only. In a word, we must appeal to the calculus of probabilities. The mechanics of gases are statistical, and the physical laws to which they lead are statistical laws. We cannot, therefore, hope to obtain laws of certainty, but only laws which are very probable or practically certain. This character of the theory, which at some periods has brought it into disfavour, should,

on the contrary, be regarded as a most suggestive one. As we shall see, it has enabled a new light to be thrown on the second law of thermodynamics, and has cleared our ideas on the fundamental nature of this principle.

Unfortunately, the extreme complication of the molecular motions brings with it a corresponding complication in the mathematical calculation which is necessary for the complete and rigorous development of the theory. This complication is such that it frequently necessitates a resort to simplifications which are sometimes hazardous as a means of pursuing the calculation. It is possible, however, to define at each stage the degree of rigour claimed, and, since by such summary procedure, we are led to results whose agreement with experiment is almost surprising, there is no reason to doubt the accuracy of the principles. In spite of difficulties we are unable to deny, it is very satisfactory on the whole that we may consider the theory as built upon foundations which are almost unassailable.

The small compass of this volume forbidding all purely mathematical developments, we shall be content to study the simplest hypotheses, for example that of elastic collisions, and to arrange the results in logical order ; in a word, to expound the sequence of ideas rather than the detail of calculations. We shall refer the reader anxious to extend his knowledge to the works mentioned in the bibliography at the end of the volume.

A few historical notes may be useful to conclude the generalities which have gone before. Physicists do not consider a theory properly scientific unless it has adequate experimental foundations. It does not appear, therefore, to be of much interest to probe classical antiquity or Greek and Roman philosophies in a search for the origin of atomistic theories. Precise knowledge of the experimental laws of the compressibility of gases dates in reality only from Boyle and Marriotte. It is only just, however, to consider Daniel Bernouilli (1730) as the founder of the modern kinetic theory ; it was he, in fact, who first explained the law of Marriotte by molecular motions. The complete development of atomism, however, only began with the discovery of the fundamental laws of chemistry, in particular the laws of Dalton, Avogadro, and Gay-Lussac, which confirmed the atomistic doctrine at the beginning of the nineteenth century. Since that time progress has been rapid. But it was principally in the middle of the nineteenth century, with Maxwell and Clausius, that the theory received the firm mathematical basis on which it rests to-day. More recently the works of Boltzmann, Kirchhoff, Van der Waals, and, among our contemporaries, those of Lord Rayleigh, H. A. Lorentz, Brillouin, etc., have given it a breadth which, going hand in hand with experimental progress, has made it one of the most vital branches of theoretical physics.

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THE KINETIC THEORY OF GASES

CHAPTER I

DISTRIBUTION OF VELOCITIES. LAWS OF PERFECT GASES

1. Molecular Structure of a Gas.—The molecules which constitute a gaseous medium should be considered as particles of extremely small dimensions, animated by rapid and unceasing movements in all directions. The movements of these particles remain sensibly rectilinear and uniform so long as they do not pass sufficiently near one another to be deflected by their mutual interactions or by their collisions. At the moment when an accidental "encounter" of this nature is produced, the velocities of the molecules concerned suffer abrupt changes in magnitude and in direction, changes the duration of which are very short compared with the time during which the molecules move freely. The trajectories of the molecules must therefore be represented as irregular broken lines, of which each element is approximately straight. Collisions of molecules with the walls of the containing vessel introduce in the trajectories perturbations of the same type as those which originate from intermolecular collision.

We shall learn to measure molecular diameters, to calculate the number of molecules contained in a given volume of the gas, as well as their velocities of translation. We shall see also that, at ordinary temperatures and pressures, molecules behave as particles of very small dimensions relative to their mutual distances, projected with velocities comparable to those of rifle-bullets, and accumulated in every element of volume of the gas in enormous numbers. The shape and structural details of the molecules naturally depend on the chemical nature of the gas considered. In a complex gaseous mixture the molecules will be of several kinds. Finally, the translatory motion that the molecule experiences as a whole does not exclude, in the general case, movements of the molecule about its centre of gravity or even internal movements of different parts of the same molecule relative to one another.

2. Distribution of Velocities : Maxwell's Law.—Let us consider a pure gas in thermal equilibrium contained in a solid envelope at a uniform temperature. We shall assume that molecular motions and collisions do not affect the molecular density of the gas, that is to say, the number of molecules n per cm^3 , and, consequently, that this density remains uniform on the average in the course of time throughout the gas. In the second place, we shall assume that, in each element of volume,* the molecules possess velocities distributed in all directions, whose magnitudes are themselves distributed according to some law independent of the

* The elements of volume with which we are concerned here are always supposed to be very small compared with the total volume of the gas, but sufficiently large to hold an immense number of molecules. This dual condition is realisable since, as we shall see, there are 2.9×10^{16} molecules per cubic millimetre of a gas under normal conditions,

position of the selected element; this law will only be modified by molecular collisions. To simplify the terminology, we shall say that the gas is in a state of molecular chaos.

The preceding hypotheses are fundamental, and indispensable for the application of probability considerations. They lead to a knowledge of the law of distribution of velocities in the state of thermal equilibrium.

If all the molecules initially possessed the same velocities, this uniformity would be destroyed immediately by collisions. With the aid of the hypothesis of molecular chaos, Maxwell has shown that, when the state of thermal equilibrium is attained, the magnitudes of the molecular velocities distribute themselves according to a law which is no longer modified by collisions. His demonstration, claiming little rigour at first, has been improved and generalised by himself, and subsequently by Boltzmann, Jeans, and others. It is valid whatever may be the complexity of molecular structure and mutual interaction. For the present we shall assume the truth of the result obtained, considering it as verified by its consequences.*

Let

$$dn = nf(u, v, w)dudvdw \quad . \quad . \quad (I)$$

be the number of molecules per cm.³ whose velocities have components comprised within the limits, u , v , w and $u + du$, $v + dv$, $w + dw$. To ascertain the law of distribution of velocities we must determine the function f . The velocity c of a molecule is often represented graphically by a point in space whose co-ordinates are equal to the components of its

* The elements of a general deduction are given in Chapter V.

velocity u, v, w ; such a point is called a velocity-point. The product $du dv dw$, therefore, represents an element of volume which may conveniently be abridged to $d\tau$. According to this, we shall be able to say that the number of molecules per cm.³ whose velocity-points lie within the element $d\tau$ is $nf(u, v, w)d\tau$, or again that the probability that one molecule should have its velocity-point in the element $d\tau$ is $f(u, v, w)d\tau$.

With this assumption the law of permanent distribution obtained by Maxwell for the state of thermal equilibrium is the following:—

$$f(u, v, w) = ae^{-b(u^2 + v^2 + w^2)} = ae^{-bc^2}.$$

a and b are constants the significance of which will appear later.

Expressing the total number of molecules per cm.³ by n , we find

$$\int f(u, v, w) du dv dw = 1,$$

the sign of integration representing a triple integral extending from $-\infty$ to $+\infty$ for each variable. Replacing f by its mathematical expression and making use of well-known mathematical formulæ,* we get the relation

$$a = \sqrt{\frac{b^3}{\pi^3}}.$$

It is convenient to replace b by hm , in which m is the mass of a molecule and h is a new constant. We may therefore put

* See Note I at the end of the volume. Formula 1.

$$a = \sqrt{\frac{h^3 m^3}{\pi^3}} \quad (2)$$

$$f(u, v, w) = \sqrt{\frac{h^3 m^3}{\pi^3}} e^{-hm(u^2 + v^2 + w^2)} \quad (3)$$

$$dn = n \sqrt{\frac{h^3 m^3}{\pi^3}} e^{-hm(u^2 + v^2 + w^2)} du dv dw \quad (4)$$

Integrating equation (4) with respect to v and w from $-\infty$ to $+\infty$, we obtain the number of molecules per cm.³ whose components of velocity parallel to a given direction Ox are comprised within the limits u and $u + du$. The result obtained,* which is frequently of service, is †

$$dn_1 = n \sqrt{\frac{hm}{\pi}} e^{-hmu^2} du \quad (5)$$

We can interpret formula (4) by saying that the probabilities that the components of velocity of a molecule shall lie between u and $u + du$, v and $v + dv$, w and $w + dw$, are independent; the probability $f(u, v, w)d\tau$ is the product of three probabilities which depend on u , v , and w respectively.

Formula (4) enables us to obtain quite easily the number dn_c of molecules whose velocities lie between c and $c + dc$, without any reference to their direction. It is sufficient to note that for these molecules, $u^2 + v^2 + w^2$ is a constant equal to c^2 , so that their number is obtained by integrating the

* See Note I at the end of the volume. Formula 1.

† The formula (5) is identical with that which Gauss has given for the Law of Errors, and which is occasionally referred to as the Law of Large Numbers. If we measure a quantity, and if u is the error in one measurement taken among a large number of others, the number dn of measurements for which the error lies between u and $u + du$ is given by formula (5).

element of volume $dudvdw$ for the whole space between spheres of radii c and $c + dc$, which is therefore $4\pi c^2 dc$. We find in this way

$$dn_c = 4n \sqrt{\frac{h^3 m^3}{\pi}} e^{-hmc^2} c^2 dc \quad . \quad . \quad (6)$$

The curve opposite (Fig. 1), which represents the

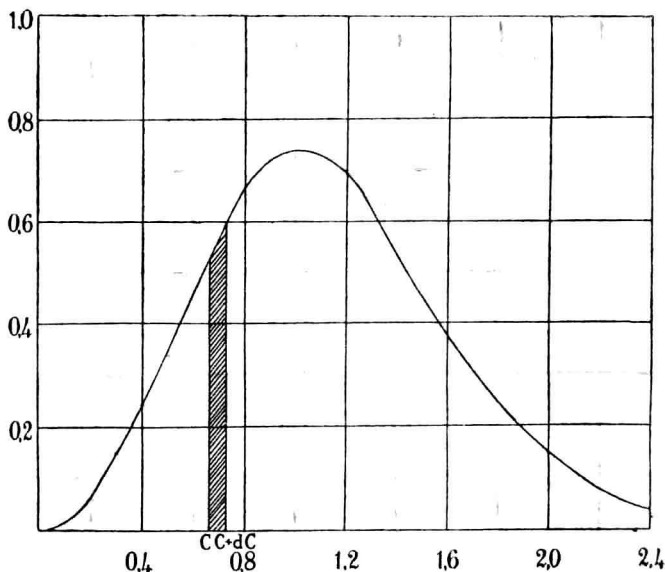


FIG. 1.

function $2x^2e^{-x^2}$, gives a concrete idea of the law of distribution of velocities: the number of velocities, the magnitudes of which lie between two neighbouring abscissæ c and $c + dc$, is proportional to the shaded area.

3. Average Velocities.—If G is any quantity whatever corresponding to a molecule, the arith-

metrical mean of the values G may take for all the molecules in a given element of volume is referred to as the mean value of this quantity in this element of volume, and is represented by \bar{G} .

Formula (6) enables us to calculate the mean square velocity, that is to say the velocity C , the square of which is equal to the average of the squares of all the velocities. We obtain actually *

$$C^2 = \bar{c^2} = \frac{1}{n} \int_0^{\infty} c^2 dn_c = \frac{3}{2hm} \quad . \quad . \quad (7)$$

This velocity C plays an important part in everything that follows, and it is important to guard against confusing it with the real mean velocity, v , given by

$$v = \bar{c} = \frac{1}{n} \int_0^{\infty} c dn_c = \frac{2}{\sqrt{\pi hm}} \quad . \quad . \quad (8)$$

or with the most probable velocity c_0 , which makes the expression (6) a maximum, and consequently has the value

$$c_0 = \frac{1}{\sqrt{hm}}.$$

We see that

$$\frac{v}{C} = \sqrt{\frac{8}{3\pi}} \quad . \quad . \quad . \quad (8a)$$

and

$$\frac{c_0}{C} = \sqrt{\frac{2}{3}}.$$

* Note I. Formula 5. The arithmetical mean of the values of c^2 , which is, rigorously speaking, an ordinary sum, has been replaced by a definite integral. This method of calculation is justified by the remark contained in the note on page 3.