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XLI. *On the Mechanical Analogue of Thermal Equilibrium between Bodies in Contact.* By G. H. BRYAN and LUDWIG BOLTZMANN*.

[Abstract.]

THE great disadvantage of the Kinetic Theory has been that it has not hitherto furnished a very satisfactory proof of the fundamental property of temperature, namely, that two bodies in contact are at *equal temperature* when neither gains or loses heat from the other.

In a medium composed of two or more different kinds of gas molecules mixed together, the conditions of equilibrium of kinetic energy involve Avogadro's well-known law†, namely, that the mean kinetic energies of translation of the different kinds of molecules shall be equal. From this we naturally infer that the quantity which represents *temperature* in the kinetic theory is proportional to the mean *vis viva* of translation. But our experimental knowledge of the properties of temperature is necessarily derived from observations of bodies which do *not* mix, and it is impossible to form a purely physical conception of the temperatures of two mixed gases apart from each other. We can only experiment on the temperature of the whole *mixture*.

It is therefore of great interest to devise a mechanical representation of the phenomena presented by two bodies between which transference of heat takes place by conduction, but whose molecules do not become indefinitely interdiffused. The system now to be described affords such a representation.

Let X and Y be two infinite parallel planes (or other surfaces) at a small distance apart, dividing space into three

* This paper is taken from a memoir by Prof. Ludwig Boltzmann and G. H. Bryan, communicated by Prof. Boltzmann to the Imperial Academy of Vienna, Dec. 13, 1894. Read at the meeting of the Physical Society, April 26, 1895.

† *Wien. Sitzungsber.* vol. lxiii. 1871, vol. lxvi. 1872, vol. xciv. 1886, vol. xcvi. 1887.

regions, S_1 , S_2 , and σ , of which the region S_1 lies to the left of X , the region S_2 lies to the right of Y , and the region σ lies between the surfaces X , Y , and may be supposed to be very thin by supposing X , Y to be very near together.

Let there be two different kinds of molecules A , B , the former represented in the figure by light, and the latter by dark points, and let these molecules be acted on by different laws of force specified as follows :—

(i) The plane Y shall be supposed to repel the A molecules with a force which vanishes at all points on the left-hand side of X , but which becomes infinitely great as we approach the plane Y itself so as to prevent any of the A molecules from crossing beyond Y and passing into the region S_2 . This force shall not act on the B molecules.

(ii) In like manner, the plane X shall be supposed to repel the B molecules with a force which vanishes at all points on the right-hand side of Y , but which becomes infinitely great as we approach the plane X itself, so as to prevent any of the B molecules from crossing beyond X and passing into the region S_1 . This force shall not act on any of the A molecules.

Then in the region S_1 we have a gas composed only of A molecules, and in the region S_2 we have a gas composed entirely of B molecules. Between these regions there is the region σ containing a mixture of both kinds of molecules, and these molecules will collide with one another, and energy will thus be transferred from the molecules of one gas to those of the other.

The conditions of equilibrium of *vis viva* can be found by the usual methods, and the proof is applicable to the more general case where the A molecules are acted on by *any* external forces and the B molecules are acted on by any other external forces independent of the former forces, the two sets of molecules being mixed in those regions where the potentials of the two sets of forces are neither of them infinite. For this purpose it is convenient to use generalized coordinates.

Let $q_1, q_2, \dots q_m$ be the generalized coordinates of an A molecule ;

$p_1, p_2, \dots p_m$, the corresponding generalized momenta ;

T_1 its *vis viva*, χ_1 its potential energy ;

$E_1 = T_1 + \chi_1$ its total energy.

Also let $Q_1, Q_2, \dots Q_n$ be the coordinates of a B molecule ;

$P_1, P_2, \dots P_n$ the corresponding momenta ;

T_2 its *vis viva*, χ_2 its potential energy ;

$E_2 = T_2 + \chi_2$ its total energy.

Then, if χ_2 is a different function of $Q_1, Q_2, \dots Q_n$ to what χ_1 is of $q_1, q_2, \dots q_m$, the forces on the two kinds of molecules will be different.

Now it is proved* that if the number of A molecules whose coordinates and momenta be within the limits of the differential,

$$dp_1 \dots dp_m dq_1 \dots dq_m$$

is proportional to

$$Ae^{-h_1 E_1} dp_1 \dots dp_m dq_1 \dots dq_m, \dots \quad (1)$$

this distribution is permanent in the absence of collisions between the molecules, and is also unaffected by collisions between two A molecules.

Similarly if the B molecules are distributed with frequency proportional to

$$Be^{-h_2 E_2} dP_1 \dots dP_n dQ_1 \dots dQ_n, \dots \quad (2)$$

this distribution is stationary in the absence of collisions between the molecules, and is unaltered by collisions between two B molecules.

* *Wien. Sitzungsber.* vol. lxxii. 1875, vol. lxxviii. 1878, vol. xcvi. 1887.

Lastly, we must consider the effect of collisions between an A molecule and a B molecule. Now if the time of duration of a collision is infinitely short, the coordinates of the colliding molecules are the same at the beginning and end of a collision. And if we consider only collisions between pairs of molecules which are in a given configuration so that the coordinates of the molecules have given values, the momenta of the colliding molecules will be distributed with frequencies respectively proportional to

$$A_1 e^{-h_1 T_1} dp_1 \dots dp_m,$$

and

$$B_1 e^{-h_2 T_2} dP_1 \dots dP_m,$$

where A_1 and B_1 are constants, the potential energies χ_1 and χ_2 being the same for all the molecules in the given configuration.

If, then, we write

$$f = A_1 e^{-h_1 T_1}, \quad F = B_1 e^{-h_2 T_2},$$

and if f' , F' be the values of the corresponding quantities after the collision, it is proved by Dr. Boltzmann * that

$$fF = f'F'; \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and since finite forces have no effect during the infinitely small time of duration of a collision, the proof is independent of the finite forces between the molecules. The last equation gives

$$e^{-h_1 T_1 - h_2 T_2} = e^{-h_1 T_1' - h_2 T_2'},$$

that is

$$h_1 T_1 + h_2 T_2 = h_1 T_1' + h_2 T_2'.$$

But by the conservation of *vis viva*,

$$T_1 + T_2 = T_1' + T_2'.$$

Multiplying by h_2 and subtracting from the previous equation, we have

$$(h_1 - h_2) T_1 = (h_1 - h_2) T_1',$$

whence, since T_1 , T_1' are not in general equal,

$$h_1 - h_2 = 0, \text{ or } h_1 = h_2. \quad . \quad . \quad . \quad . \quad (4)$$

* *Wien. Sitzungsber.* vol. lxvi. 1872, last part.

The mean *vis viva's* of the A and B molecules are $3/2h_1$ and $3/2h_2$ and are therefore equal.

In my Report to the British Association I suggested that the distribution of a large number of molecules of the same or different kinds in which the coordinates (q) and momenta (p) are so arranged that the number of molecules in the neighbourhood of any given state is proportional to

$$e^{-hE} dp_1 \dots dp_n dq_1 \dots dq_m, \dots \dots \dots (5)$$

h being the same for all kinds of molecules, be called *The Boltzmann-Maxwell Distribution*, the law which asserts the permanency of the Boltzmann-Maxwell distribution in any particular case being called *The Boltzmann-Maxwell Law*.

If these names be adopted, we have the result that the Boltzmann-Maxwell Law holds good for a mixture of different kinds of gas molecules, even when the forces which act on the molecules of one gas are entirely different from those which act on any other gas. The reasoning applies equally when there are any number of different kinds of molecules.

The densities of the A and B molecules are respectively proportional to

$$Me^{-h\chi_1} \text{ and } Ne^{-h\chi_2}, \dots \dots \dots (5)$$

where M and N are certain constants depending on the total numbers of respective molecules.

Hence if $\chi_1 = \infty$ over any region, that region contains only B molecules, and if $\chi_2 = \infty$ the region contains only A molecules, and the two kinds of molecules are mixed together in regions where χ_1 and χ_2 are both finite.

Instead of assuming a field of force of the kind considered above, we might assume the A molecules to be positively electrified and the B molecules to be negatively electrified, the planes X, Y being kept at a constant difference of potential. If this difference of potential be V and if the charges on the respective molecules are $q_1 - q'$, the densities of the A molecules in the regions $S_1 S_2$ will be in the ratio of $1 : e^{-hqq'V}$, and the densities of the B molecules in the ratio of $e^{+hqq'V} : 1$ and by making V sufficiently great we shall make $e^{-hqq'V}$ and $e^{-hqq'V'}$ very small, and the gases in the regions S_1, S_2 will be very nearly pure.

If collisions are replaced by encounters in which the molecules attract or repel one another with finite forces during a finite time, the same result may be proved by a method indicated by Prof. Boltzmann in his recent communication to the British Association, entitled "On the Application of the Determinantal Relation to the Kinetic Theory of Polyatomic Gases" *.

For the determinantal relation between the multiple differentials of the coordinates and momenta of a conservative dynamical system at the beginning and end of any interval of time $t' - t$ is of the form

$$\frac{\partial(p_1', \dots p_m', q_1', \dots q_m')}{\partial(p_1, \dots p_m, q_1, \dots q_m)} = 1. \dots \dots (6)$$

(1) If we apply this relation to a single molecule of gas moving about freely or in a field of external force, the relation will apply so long as the molecule considered does not encounter or collide with other molecules; and the possible laws of permanent distribution of the coordinates and momenta among a large number of such molecules may now be established thus:—

We know that for any one molecule the total energy is independent of the time or

$$E_1 = \text{constant},$$

and the determinantal relation shows that the multiple differential

$$dp_1, \dots dp_m dq_1, \dots dq_m$$

is also independent of the time.

Therefore, if the law of distribution be such that the number of molecules included within the limits of the multiple differential at any instant of time (t) is

$$f_1(E_1) dp_1 \dots dq_m, \dots \dots \dots (7)$$

where f_1 denotes any function whatever, the same law will hold good at any subsequent instant of time (t').

In particular, taking $f_1(E_1) = e^{-hE_1}$, we conclude that in the absence of such encounters any distribution determined by the expression (1) of the A molecules will be permanent, and

* Oxford Report, p. 102.

a similar conclusion holds with respect to the distribution (2) of the B molecules.

(2) We may take as our dynamical "system" a pair of molecules of the same or different kinds in the course of a binary encounter, it being assumed that the intermolecular forces remain finite during encounter, and that at each instant there are sufficient encounters of the same kind to give rise to a law of permanent distribution among the encountering sets of molecules. Here the multiple differential will have to include all the coordinates and momenta of all the molecules in the group considered. Hence if E is the total energy of a pair of A and B molecules in the course of an encounter, any distribution of the pairs of molecules of the form

$$f(E) dp_1 \dots dp_m dq_1 \dots dq_m dP_1 \dots dP_n dQ_1 \dots dQ_n$$

will be permanent so long as the molecules of any one pair do not encounter any molecules not in that pair.

But in a gas each molecule will encounter various molecules in succession, so that the same pair of molecules cannot be considered permanently as a system apart from the rest. From this we find at once that if the frequency of distribution f is a function of energy alone, it *must* be of the well-known form

$$f = e^{-hE}.$$

For *before* two molecules encounter each other, the frequency of distribution of the coordinates and momenta of one cannot depend on the coordinates and momenta of the other. Hence if f_1, f_2 denote the frequencies of distribution of the two molecules just before the encounter,

$$f_1 \times f_2 = f(E).$$

Now we may write

$$E = T_1 + T_2 + \chi_1 + \chi_2 + \chi_{12},$$

where T_1, T_2 are the kinetic energies of the two molecules, χ_1, χ_2 are the potential energies of the molecules due to the field of force, χ_{12} their mutual potential energy during the encounter.

But the same law must hold just before the encounter as during it, and just before the encounter χ_{12} is zero, so that

$$E = E_1 + E_2,$$

where E_1 E_2 are the separate energies of the molecules ; and the resulting relation

$$f_1 \times f_2 = f(E_1 + E_2) (8)$$

can only be satisfied by

$$f_1 = e^{-hE_1}, \quad f_2 = e^{-hE_2}, \quad f = e^{-hE}.$$

Hence before and after the encounter the molecules have their coordinates and momenta distributed with frequencies proportional to e^{-hE_1} and e^{-hE_2} respectively. But *during* an encounter the frequency of distribution of *all* the coordinates and momenta of the pair or group is proportional to e^{-hE} , and the two encountering molecules cannot be considered separately.

For a pair of molecules we may write the function

$$\begin{aligned} f &= e^{-h(T_1 + \chi_1 + T_2 + \chi_2 + \chi_{12})} \\ &= e^{-hT} \times e^{-hT_2} \times e^{-h(\chi_1 + \chi_2 + \chi_{12})} (9) \end{aligned}$$

This shows that for any given *configuration* the *momenta* of the molecules denoted by the suffixes 1, 2 are separately distributed with frequencies proportional to e^{-hT_1} and e^{-hT_2} respectively. The distribution of the *coordinates* of one molecule is not, however, independent of the position of the other owing to the presence of the factor $e^{-h\chi_{12}}$. When the encounter is over χ_{12} vanishes, this factor disappears, and the distributions of the coordinates of the two molecules become independent of each other, being of the forms (1) (2).

And since χ_1 and χ_2 may be of any forms whatever, and may be entirely different, the reasoning is immediately applicable to systems such as that which forms the subject of the present paper. Wherever χ_1 or χ_2 becomes infinite the number of molecules becomes zero, so that encounters do not there occur.

Similar reasoning holds good for encounters between two A molecules or between two B molecules or for simultaneous encounters between any number of molecules, provided that the encounters considered are sufficiently frequent to *have* a law of distribution.

And of course collisions can be treated as a limiting case of encounters.

The above brief investigation shows the advantage of applying the determinantal relation to encounters as well as to the free motion of molecules between encounters. With this method it is not necessary to start as Prof. Boltzmann previously did, by *assuming* the frequency of distribution to be determined by a function f of the form e^{-hE} , but if we merely assume f to be any function of the energy we may deduce that the form $f(E) = e^{-hE}$ is *necessary* as well as *sufficient*.

XLII. *Note on a Neglected Experiment of Ampère.*

By SILVANUS P. THOMPSON*.

IN the year 1822 Ampère, being at Geneva, showed to De la Rive in his laboratory a number of his now classical experiments on the actions of conductors carrying currents upon other conductors and upon magnets. These are recounted by A. De la Rive in the *Annales de Chimie et de Physique*, xxi. p. 24 (1822).

Amongst these experiments there is one that has almost been forgotten, but which, had it been followed up, would assuredly have led Ampère to anticipate by some years the great discovery of Faraday as to the induction of currents.

The experiment was first described by Ampère in October 1821, in a letter† to Van Beck. It had been tried in the preceding July. The following is Ampère's own first description of it:—

“Ce que cette expérience prouve directement, c'est que la proximité d'un courant électrique n'en excite point, par influence, dans un circuit métallique de cuivre, même dans les circonstances les plus favorables à cette influence. Voici l'expérience que je fis alors pour m'en assurer : je formai avec un long fil de cuivre A B C D E F [fig. 1], revêtu d'un ruban, une spirale B C D E dont les tours étaient séparés les

* Read April 26, 1895.

† *Journal de Physique*, t. xciii. p. 447, Oct. 1821. Reprinted at p. 212, vol. ii. of the 'Collection de Mémoires relatifs à la Physique, publiés par la Société française de Physique,' 1885.