XX.—On the Partition of Heat Energy in the Molecules of Gases.
By Dr Paul Ehrenfest. (*Communicated by* Dr W. PEDDIE.)

IN a paper published some time since,* Mr Peddie takes up the following question : Given a gas whose molecules contain atoms which are held together by purely elastic forces, do there exist, even in this simplest type of multiply-atomic molecules, cases in which, when there is equilibrium of heat, the average equipartition of kinetic energy demanded by the Boltzmann-Maxwell Law does not exist ?

Mr Peddie's formulation of the question possesses, above all, the merit of having directed the discussion of the Boltzmann-Maxwell Law of energy partition to a case which adapts itself readily to calculation. This discussion of elastically oscillating systems assumes a special interest in regard to the difficult problem of the partition of energy between ether and matter.

Having in view the great importance which, in this way, this formulation of the question possesses, I propose to show—

1. There actually exist, in the sense of the general question, a class of cases in which elastically oscillating systems certainly exhibit non-equipartition. These cases are obtained by means of special *simultaneous* assumptions: (*a*) regarding the mechanical structure of the oscillating molecule ; (*b*) regarding the character of the collisions amongst the molecules. But this class of non-equipartition cases does not contradict Boltzmann's line of thought. It verifies, rather, certain restricting remarks which, without developing them farther, Boltzmann made in his first work on the H-theorem.

2. Mr Peddie seeks, in the special development of his work, to construct an essentially different class of non-equipartition cases. Their existence would in fact be irreconcilable with Boltzmann's results. Yet, as I shall show farther on, this special presentment, at least in its present form, does not suffice to prove the existence of the second class of non-equipartition cases.

It would thus appear that *the construction, postulated by Mr Peddie for elastically oscillating molecules which do not exhibit equipartition,*

* W. Peddie, "On Vibrating Systems which are not subject to the Boltzmann-Maxwell Law," *Proc. Roy. Soc. Edin.*, vol. xxvi. 1906 (pp. 130–141).

can in fact be carried out in a somewhat modified manner. But this construction then forms no objection to Boltzmann's general line of thought.

§ 1. Boltzmann has given, in §§ 74–86 of the second volume of his *Gastheorie*, on the basis of the H-theorem, the theory of the equilibrium of heat in multiply-atomic gases. We shall frequently refer in what follows to this presentation. Boltzmann makes the following remarks in preface to the deduction of the law of distribution (page 241):—"The complete development of the proof that the distribution, $\epsilon^{-h \cdot \text{Energy}}$, is the only possible one which can maintain itself in a stationary gas, whose molecules are multiply-atomic, has not hitherto been successful in complete generality. Yet the development of this proof is possible, in the simplest and practically most important cases, to the same extent as for mon-atomic gases."

The deduction of the distribution from the H-theorem involves two distinctly separate steps :—

A. The deduction of the known equation

$$f_1 f_2 = f_1^1 f_2^1 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

(see §§ 74–82).

B. The solution of this (functional) equation. Whilst this second step is very simple in the case of monatomic molecules, it offers special difficulty in the case of multiply-atomic molecules. (For the discussion of particular cases, see Boltzmann in §§ 83–86.) But, at the same time, this second step exhibits the possibility, *e.g.* through special assumptions regarding the nature of the collisions between the molecules, of finding cases of non-equipartition.

§ 2. Each molecule is made up of atoms A, B, C . . . . With reference to the nature of the collisions between the molecules, Boltzmann follows out two essentially different assumptions.

Assumption I.—Every atom of every molecule can collide with every other (§§ 83–84).

Assumption II.—In each molecule the atom A alone is susceptible of collision ; the remaining atoms are influenced only through the changes of motion of the atoms A.

In the case of assumption I., the H-theorem furnishes a complete estimation of the speed distribution for atoms of all kinds. As well the atoms A, as B, as C, ... , obey Maxwell's speed distribution, and certainly are such that the mean kinetic energy (time, and number, mean), for the atoms of all kinds, has the same value (p. 243).

In the case of Assumption II., *on the contrary, the H-theorem furnishes too few equations, apart from supplementary assumptions, for the deter-*

mination of the speed distribution of all atoms (p. 246). In connection with this point, the calculation is carried out for diatomic molecules in the case in which A and B act upon each other in the direction of the central line, and only the atoms A strike each other. In this special case we can so complete the result of the H-theorem, by apparently plausible assumptions, that there results a fixed speed distribution. It appears that here also, both for A and B, Maxwell's distribution law holds, and certainly that the mean kinetic energy (time, and number, mean) has the same value.

§ 3. The calculation by which, in this special case, Boltzmann reached the result, does not settle whether the same result would hold in somewhat more general cases, *e.g.* for a molecule with more than two atoms or with another law of force. But the calculation which Boltzmann carried out in § 86 for the two-planet case can be put in a somewhat more general form. This shows at once that, in the case of assumption II., for observance or non-observance of equipartition, it is very essential, on account of the structure of the molecule, that the *free* motion (between two collisions) admit an integral of the form

$$f(\xi_4, \ldots \xi_{3n}, \dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3 \ldots \dot{\xi}_{3n}) = \text{const.}, \qquad . \qquad . \qquad (2)$$

that is to say, an integral which does not depend explicitly either on the time, or the velocity components $\dot{\xi}_1$, $\dot{\xi}_2$, $\dot{\xi}_3$, of the atom A.[*] The farther pursuit of this question leads, then, to a corresponding systematic determination of non-equipartition cases. For the present purpose, it suffices to give one case. We choose one such which furnishes the immediate answer to Mr Peddie's question.

§ 4. We consider a mixture of two gases of the following nature. The molecules of the first gas are monatomic, and do not act upon each other with any force (except on collision). The molecules of the second gas are constituted of n atoms A, B, . . . which are bound together, and to their equilibrium position, by elastic forces. Here also the atoms A alone are to suffer blows, and these can come from the freely moving molecules of the first kind.

The cartesian co-ordinates of the n-atoms, measured from the equilibrium position of each atom, may be denoted throughout by

$$\xi_1, \xi_2, \ldots, \xi_{3n},$$

where ξ_1, ξ_2, ξ_3, are the co-ordinates of the atom A. As elastically oscillating

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[1] Moreover, it can then be shown that the integral does not contain the co-ordinates ξ_1, ξ_2, ξ_3. For the proof, one has to use the supposition that the forces depend only on the co-ordinates.

systems, the molecules of the second kind possess $3n$ normal-vibrations. The normal co-ordinates may (in arbitrary order) be denoted by

$$X_1, X_2, \ldots, X_{3n}.$$

For the kinetic and potential energies we have the following representations:

$$2T = \sum_1^{3n} m_h \dot{\xi}^2{}_h = \sum_1^{3n} \dot{X}^2{}_i \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2V = \sum_1^{3n} \sum_1^{3n} \beta_{hk} \xi_h \xi_k = \sum_1^{3n} B_i X^2{}_i \quad . \quad . \quad . \quad . \quad (4)$$

There are, farther, the following substitutions:—

$$\left.\begin{aligned}
X_1 &= l_{11}\xi_1 + l_{12}\xi_2 + l_{13}\xi_3 + \ldots + l_{1, 3n}\xi_{3n} \\
X_2 &= l_{21}\xi_1 + \quad \ldots \\
&\ldots \ldots \ldots \\
X_{3n} &= l_{3n, 1}\xi_1 + \quad \ldots \quad + l_{3n, 3n}\xi_{3n}
\end{aligned}\right\} \quad . \quad . \quad (5)$$

The substitution coefficients l_{ih} depend on the mechanical structure of the molecule. We make now the following special assumption regarding this structure. Postulate that

$$l_{11} = l_{12} = l_{13} = 0 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

All other coefficients l_{ih} shall have any values, different from zero, so far as they are compatible with positive values of m and real values of β_{hk}. The physical meaning of this assumption is this:—

In the expression for the energy connected with the first normal vibration

$$E_1 = \tfrac{1}{2}(\dot{X}^2{}_1 + B_1 X^2{}_1), \quad . \quad . \quad . \quad . \quad (7)$$

the speed components $\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3,$ *of the atom A do not appear* (nor also its co-ordinates).

5. One sees easily now that this assumption regarding the structure, together with the restricting assumption regarding the collisions, brings in non-equipartition.

To this end we show next that the quantity E_1 retains for each molecule its original value (E_1 is an integral of the type defined in equ. 2).

(*a*) During the free motion the quantities $E_1, \ldots, E_{3n}$ remain constant.

(*b*) E_1 also does not change by the blows. For the quantities

$$\dot{\xi}_4, \ldots, \dot{\xi}_{3n}, \xi_1, \ldots \xi_{3n}$$

possess immediately after the blow the same values as they had immediately before the blow. Only the quantities

$$\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3$$

suffer certain sudden changes. But, since the quantities $\dot{\xi}_1, \dot{\xi}_2, \dot{\xi}_3,$ do not

enter into E_1, that quantity possesses, immediately before and after the blow (therefore in general always), the same value.

We consider at present the simplest case: E_1 originally zero for all molecules. It remains then lastingly zero, and with it also the value of $\dot{X}_1{}^2$. So the mean value of $\dot{X}_1{}^2$ taken over all molecules is lastingly zero.

$$\overline{\dot{X}}{}^2_1 = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

however one may change the temperature of the first gas.*

On the other hand, the law of equipartition would demand that

$$\overline{\dot{X}}{}^2_1 = \overline{\dot{X}}{}^2_2 = \ldots = \overline{\dot{X}}{}^2_{3n} = a . T \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

for, according to (3), the kinetic energy is made up of sums of squares of $\dot{X}_i$, which are the so-called "momentoids" (Boltz., b. ii. § 33).

For certain questions it would be interesting to settle: Does this manifest non-equipartition for the momentoid $\dot{X}_1$ necessitate that non-equipartition holds also for $\sqrt{m_h}\dot{\xi}$? To be able to deduce this consequence, one must exclude all the special structures, which, besides the integral $E_1 = \text{const.}$, admit other integrals of the form (2). Yet that would lead as far. It is sufficient for the preceding object to settle that at any rate *the momentoid* $\dot{X}_1$ *no longer complies with the law of equipartition.* Throughout, it is essential for the attainment of the result that we make the assumption, previously taken into consideration by Boltzmann, regarding the limitation of the collisions.

If one, on the contrary, made regarding the blows the assumption I., *the H-theorem would give equipartition for both series of momentoids* ($\sqrt{m_h}\dot{\xi}_h$ *and* $\dot{X}_i$).

§ 6. We pass now to the consideration of the test of that class of non-equipartition cases which, in the introduction, we denoted as the second class of non-equipartition cases. Apart from making an assumption regarding the limitation of the blows to the atom A, equipartition can only be excluded by an assumption regarding the structure of the oscillating molecule.

We make now the assumption that the frequencies of the 3_n normal vibrations possess distinct values $p_1, \ldots, p_{3n}.$† We have

$$X_i = A_i \sin p_i(t + t_i) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (10)$$
$$\dot{X}_i = p_i A_i \cos p_i(t + t_i) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

* One can also proceed from any other original value of $\dot{E}_1$. Only one must then specially prove first that $\overline{\dot{X}}_1{}^2$ remains constant with E_1. There exists here an analogy to the case of rigid molecules with rotational symmetry.

† In § 8 this restriction will be removed.

There subsist farther the substitutions *

$$\left.\begin{array}{l} \xi_1 = a_{11}X_1 + a_{12}X_2 + \ldots + a_{1,\,3n}X_{3n} \\ \xi_2 = a_{21}X_1 + \ldots \ldots \ldots \ldots \\ \ldots \ldots \ldots \ldots \ldots \ldots \\ \xi_{3n} = a_{3n,\,1}X_1 + \ldots \ldots + a_{3n,\,3n}X_{3n}. \end{array}\right\} \quad . \quad . \quad . \quad (12)$$

with analogous substitutions for $\overset{\,\prime}{\xi}_h$. We introduce now the following time average symbol

$$\left\{ m_h\xi^2{}_h - m_k\xi^2{}_k \right\} = \frac{1}{\theta}\int_0^\theta (m_h\xi^2{}_h - m_k\xi^2{}_k)dt \quad . \quad . \quad . \quad (13)$$

Here θ denotes a time which is large relatively to the longest of the periods of the normal vibrations. The integration is extended over a free motion of the molecule of the second kind. We shall correspondingly make for the following application, the assumption that a molecule of the second kind makes numerous oscillations between two collisions.† From the assumption that all frequencies, p_i, are different from each other, it follows that

$$\{\dot{X}_i\dot{X}_j\} = 0 \qquad \text{for } i \neq j \quad . \quad . \quad . \quad . \quad (14)$$

On the other hand we have

$$\{\dot{X}_i^2\} = \frac{p^2{}_iA^2{}_i}{2}. \quad . \quad . \quad . \quad . \quad (15)$$

One has also, for the difference of the time averages of the kinetic energies $\frac{1}{2}m_h\dot{\xi}_h^2$ and $\frac{1}{2}m_k\overset{\,\prime}{\xi}_k^2$ the expression

$$\{m_h\dot{\xi}^2{}_h\} - \{m_k\overset{\,\prime}{\xi}^2{}_k\} = \frac{1}{2}\sum_1^{3n}{}_i\, p^2{}_iA^2{}_i(m_ha^2{}_{hi} - m_ka^2{}_{ki}) \quad . \quad . \quad (16)$$

The quantities

$$P^i{}_{hk} = m_ha^2{}_{hi} - m_ka^2{}_{ki} \quad . \quad . \quad . \quad . \quad (17)$$

are determined by the structure of the molecule, the quantities $A^2{}_i$ by the occasional excitation.

One can now put the question ‡—Is it possible so to choose the structure of the molecule, that is, the quantities $m_1 \ldots m_{3n}$ and β_k, that, at least for *one* pair of indices h, k, all the $3n$ quantities P shall satisfy

$$P^i{}_{h,k} > 0 \qquad i = 1, \ldots, 3n \quad . \quad . \quad . \quad (18)$$

Let us assume that this might actually be possible. Then, from equation (16), for each arbitrary excitation (for each value of the quantities $A_1 \ldots A_{3n}$) we would have

$$\{m_h\dot{\xi}^2{}_h\} > \{m_k\overset{\,\prime}{\xi}^2{}_k\}, \quad . \quad . \quad . \quad (19)$$

* Here, naturally, the earlier assumptions regarding l_{11}, l_{12}, l_{13} are no longer made.
† *Cf.* Peddie, *l.c.*, § 13.
‡ *Cf.* Peddie, *l.c.*, §§ 2, 3, 13, 14.

and only in the case of rest ($A_1 = A_2 \ldots \ldots = A_{3n} = 0$) would both expressions be simultaneously zero. Let us use farther

$$\overline{\{m_h \dot{\xi}^2{}_h\}} \qquad \qquad \qquad (20)$$

to denote the number average of the time average, taken over all molecules of the second kind.

For molecules of such structure, if they could exist, equipartition for the momentoids $\sqrt{m_h}\dot{\xi}_h$ would never occur, even with arbitrary collisions throughout. Equipartition would demand

$$\overline{\{m_h \dot{\xi}^2{}_h\}} = \overline{\{m_k \dot{\xi}^2{}_k\}} \qquad \qquad \qquad (21)$$

which, according to 19, cannot occur.

To attain, free from contradiction, to a specification of molecules of such structure, would, moreover, be to contradict a much more fundamental consequence of Boltzmann's theory, which says: Given a multitude of multiply-atomic molecules, of arbitrary structure, which obeys the law of distribution $\epsilon^{-h \cdot \text{Energy}}$, equipartition holds *for every system of momentoids* (Boltzmann, *Gasth.*, b. ii. § 42). For the molecules here discussed there is no distribution which can permit of equipartition for the momentoids $\sqrt{m_h}\dot{\xi}_h$.

§ 7. Having regard specially to this contradiction of one of the weightiest fundamental laws of Boltzmann's theory, I would show in what follows that the $3n$ inequalities (18) can never be fulfilled simultaneously. If, by means of the substitutions (12), the kinetic energy

$$T = \tfrac{1}{2} \sum_{1}^{3n} m_h \dot{\xi}^2{}_h \qquad \qquad \qquad (22)$$

be transformed to the form

$$T = \tfrac{1}{2} \sum_{1}^{3n} \dot{X}^2{}_i \qquad \qquad \qquad (23)$$

the quantities a_{hi} must satisfy the following orthogonal conditions,

$$\sum_{1}^{3n} m_h a^2{}_{hi} = 1 \qquad i = 1, \ldots, 3n \qquad \qquad (24)$$

and

$$\sum_{1}^{3n} m_h a_{hi} a_{hj} = 0 \qquad i \neq j; \left. \frac{i}{j} \right\} = 1, \ldots, 3n \qquad (25)$$

But, from (24) and (25) it follows that *

$$m_h \sum_{1}^{3n} a^2{}_{hi} = 1 \qquad h = 1, \ldots, 3n \qquad \qquad (26)$$

and

$$\sqrt{m_h m_k} \sum_{1}^{3n} a_{hi} a_{ki} = 0 \qquad h \neq k; \left. \frac{h}{k} \right\} = 1, \ldots, 3n \qquad (27)$$

* To see this readily, one introduces new quantities $j_{hi} = \sqrt{m_h} a_{hi}$.

Equations (26) give (see eq. 16) the relation

$$\sum_{1}^{3n} P^i_{hk} = 0 \qquad . \qquad . \qquad . \qquad . \qquad (28)$$

for each pair of indices h, k. *Therefore the $3n$ inequalities* (18) *can never be satisfied simultaneously, and the system postulated in* § 6 *cannot exist.*

We remark further, that the conclusion of this paragraph, and also equation (28), are independent of the frequencies p_i being different from each other, or some of them being equal.

§ 8. Equations (28) and (16) show farther: If equipartition exists for the momentoids $\dot{X}_1, \ldots \dot{X}_{3n}$, and all the frequencies p_i are different from each other, equipartition also holds for the momentoids $\sqrt{m_h}\dot{\xi}_h$.

For if

$$\overline{\{\dot{X}^2\}} = \overline{\{\dot{X}^2_2\}} = \ldots = \overline{\{\dot{X}^2_{3n}\}}, \qquad . \qquad (29)$$

i.e. if

$$p^2_1 A^2_1 = p'^2_2 A^2_2 = \ldots = p^2_{3n} A^2_{3n}, \qquad . \qquad . \qquad (30)$$

equations (16) and (28) give

$$\overline{\{m_1 \dot{\xi}^2_1\}} = \overline{\{m_2 \dot{\xi}^2_2\}} = \ldots = \overline{\{m_{3n} \dot{\xi}^2_{3n}\}} \qquad . \qquad (31)$$

The case in which not all the p_i are different from each other requires some complementary presumptions. Take, *e.g.*, $p_1 = p_2$. Then the relation (14) no longer suits for $i = 1, j = 2$. We have instead

$$\{\dot{X}_1 \dot{X}_2\} = A_1 A_2 \cos \phi_{12} \qquad . \qquad . \qquad . \qquad (32)$$

where ϕ is the phase-difference between the two fundamental oscillations X_1, X_2, which remains constant during the free motion. In order to arrive at equation (16) again, we make the farther assumption regarding the distribution, that

$$\overline{A_1 A_2 \cos \phi_{12}} = 0 \qquad . \qquad . \qquad . \qquad . \qquad (33)$$

It is always fulfilled if the distribution referred to allows contrary phase differences to occur, with equal frequency, in the various molecules. But assumption (33), together with (29), then leads to equation (31) in the case of partly equal frequencies also. *Consequently it is possible to arrange equipartition for every structure of the vibrating molecules, between every set of momentoids.*

§ 9. The above discussion is intentionally confined to the two definite questions which were formulated in the introduction; for my intention in this connection was merely to refer to the restricting remarks which Boltzmann himself made on the H-theorem. On this account the remaining questions and objections which have recently been formulated in reference to the equipartition law can be left aside in the meantime.