



LXV. On the conditions necessary for equipartition of energy

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The only consideration which is opposed to this view is the existence of polonium. The radiations of this body resemble closely the non-separable radioactivity of uranium, both in penetrating power and the absence of deviable rays. But all attempts (Soddy, *loc. cit.*) have so far failed to separate polonium from uranium, and until this is done its existence does not of itself affect the present question.

It seems as if a more satisfactory explanation of the residual activities common to both uranium and thorium, and of the connexion between the emanating power and radioactivity of ThX, is obtained on the modified view. But further work, both on this latter point and on the nature of polonium, must be awaited before the connexion between radioactivity and chemical change can be considered exactly determined.

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LXV. *On the Conditions necessary for Equipartition of Energy.*

By J. H. JEANS, B.A., *Isaac Newton Student and Fellow of Trinity College, Cambridge* *.

Introduction.

§ 1. **T**HE object of the present paper is, firstly, to give a proof of Boltzmann's Theorem on the Equipartition of Energy from a somewhat new point of view; and, secondly, to examine what are the precise conditions under which equipartition will take place, and whether these conditions are such as will occur in an actual gas.

At the outset it must be explained that the equations leading to the law of distribution admit of a simple hydrodynamical interpretation in generalized space of n -dimensions. I have made use of the hydrodynamical analogy for two reasons. In the first place it is easier to think in terms of generalized space than in terms of multiple integrals; and in the second place the terminology and results of hydrodynamics being ready to hand, a great deal of obscurity and repetition may be saved by starting at once from the hydrodynamical standpoint. So long as we only use hydrodynamical results and conceptions which have a mathematical (as opposed to a physical) basis, there will be no danger of a faulty "argument by analogy."

* Communicated by the Author.

The General Dynamical Theorem.

§ 2. Let us begin by considering the motion of a very great number of exactly similar dynamical systems, the systems being supposed for the present not to influence the motion of one another. We shall ultimately take such a system to be a molecule of a gas.

Let us suppose the configuration of this system determined by n coordinates

$$q_1, q_2, \dots q_n, \dots \dots \dots (1)$$

and let the corresponding momentoids be

$$p_1, p_2, \dots p_n, \dots \dots \dots (2)$$

Now imagine a space of $2n$ dimensions, these dimensions corresponding to all possible values of the $2n$ independent variables

$$q_1, q_2, \dots q_n, p_1, p_2, \dots p_n, \dots \dots (3)$$

Then the configuration and rate of change of configuration of any system can be represented completely and uniquely in this generalized space by a single representative point*.

Instead of saying that a system is *in the phase* $(q_1, q_2, \dots p_1, p_2, \dots)$, we shall say that it is at the point $(q_1, q_2, \dots p_1, p_2, \dots)$, of our generalized space. Let us suppose that the number of systems of which the coordinates of the representative points lie between

$$\begin{aligned} & q_1, q_2 \dots p_1, p_2 \dots \dots \\ \text{and} & q_1 + dq_1, q_2 + dq_2 \dots p_1 + dp_1, p_2 + dp_2 \dots \dots \\ \text{is} & \bar{f}(q_1, q_2, \dots p_1, p_2 \dots) dq_1, dq_2, \dots dp_1, dp_2 \dots \end{aligned}$$

This is the number of representative points which occupy the element of volume $dq_1 dq_2 \dots dp_1 dp_2 \dots$ of our generalized space. We may, therefore, speak of $\bar{f}(q_1 q_2 \dots p_1 p_2 \dots)$ as the *density* at the point $q_1 q_2 \dots$, and shall, for the sake of convenience, denote it by ρ .

§ 3. If we are given the values of the $2n$ coordinates of scheme (3) at any instant we shall be able, from a knowledge of the energy-function of the system, to calculate the values

* It will tend to clearness of thought to imagine infinite space, so that all the coordinates can range from $+\infty$ to $-\infty$. If the coordinates are not uniquely defined from the configuration (*e.g.* if q_1 is an angle so that for a given configuration q_1 may have any of the values $\phi_0, 2\pi + \phi_0, 4\pi + \phi_0 \dots$ &c.) we may either suppose just sufficient of the space taken to give only one possible value of each coordinate inside the space, or we may suppose one representative point for every possible system of values of the coordinates, so that the arrangement of points in our generalized space is periodic.

of these coordinates at any subsequent instant, so long as the system is not acted upon by any forces which are not included in the energy-function. In this way we find a "path" in the generalized space which is described by the system in question. In this way we may map out the whole of our generalized space into "stream-lines." It is obvious that there will be one, and only one, stream-line through every point of this space, and that stream-lines which are adjacent at one point remain adjacent throughout their whole course. The motion of the representative points may, therefore, be replaced by a hydrodynamical motion, this motion being continuous as regards both space and time.

Let us denote differentiation with respect to a fixed point in this space by d/dt , that with respect to a moving element by D/Dt .

The velocity at any point is, under all circumstances, a function of the coordinates only. The *necessary and sufficient* condition for a steady state is therefore

$$\frac{d\rho}{dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From the hydrodynamical equation of continuity,

$$\frac{d\rho}{dt} = \frac{D\rho}{Dt} - \sum_{(2n)} \frac{\partial \rho}{\partial \xi} \frac{\partial \xi}{\partial t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where ξ is any one of the $2n$ coordinates of scheme (3), and the summation extends to all.

Now the molecules which at any given instant occupy the element of volume $dq_1 dq_2 \dots$ will be precisely those which at some subsequent instant will occupy some other element $dq_1' dq_2' \dots$, and, by a known theorem,

$$dq_1 dq_2 \dots = dq_1' dq_2' \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In terms of our present notation equation (6) may be expressed concisely in the form

$$\frac{D\rho}{Dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence from equation (5) the condition for a steady state is seen to be

$$\sum_{(2n)} \frac{\partial \rho}{\partial \xi} \frac{\partial \xi}{\partial t} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

§ 4. Let the total energy of the system, supposed expressed in the Hamiltonian form, be denoted by E . The energy includes the potential and kinetic energies of the system. It

may include the potential energy of the system in a permanent field of force, if such exists, and it may include electrostatic or electrodynamic energies, or any other energies which are such that the equations of motion may be derived from the function E in the Hamiltonian manner. The equations of the system are $2n$ in number, being of the forms

$$\left. \begin{aligned} \frac{\partial q_r}{\partial t} &= \frac{\partial E}{\partial p_r} \dots (r=1, 2, \dots n) \\ \frac{\partial p_r}{\partial t} &= -\frac{\partial E}{\partial q_r} \dots (r=1, 2, \dots n) \end{aligned} \right\} \dots \dots (9)$$

The elimination of t from these equations will give the equations of the stream-lines which determine the paths of the representative points in our generalized space. These equations will be $2n-1$ in number, and will be capable of expression in the forms

$$\psi_s = \text{constant} \quad (s=1, 2, \dots 2n-1), \dots \dots (10)$$

where ψ_s is a definite function of the $2n$ coordinates*.

There is one further equation which can be derived from equations (9), and this may be expressed in the form

$$\psi_{2n} = \text{constant} + f(t), \dots \dots \dots (11)$$

where ψ_{2n} is a function of the $2n$ coordinates. This last equation determines the motion of the particles along the stream-lines. The $2n$ equations (10) and (11) are the exact equivalents of the $2n$ equations (9).

Now let us transform coordinates in our generalized space, from the coordinates of scheme (3) to the generalized coordinates

$$\psi_1, \psi_2, \dots \dots \psi_{2n-1}, \psi_{2n} \dots \dots \dots (12)$$

Transformed into these coordinates equation (8) becomes

$$\sum_{s=1}^{s=2n} \frac{\partial \rho}{\partial \psi_s} \frac{\partial \psi_s}{\partial t} = 0. \dots \dots \dots (13)$$

For the first $(2n-1)$ values of s ($s=1, 2, \dots 2n-1$) we have

$$\frac{\partial \psi_s}{\partial t} = 0.$$

* From another point of view equations (10) may be regarded as first integrals of the equations of motion. The whole question turns on the fact that the equations are $2n-1$ in number. That this is so is evident from the fact that the path of every point must be definitely and uniquely determined by them.

If we exclude (as we legitimately may) the case of systems which remain permanently at rest in an equilibrium configuration, it follows that we must have $\frac{\partial \psi_{2n}}{\partial t}$ different from zero. Hence equation (13) assumes the form

$$\frac{\partial \rho}{\partial \psi_{2n}} = 0,$$

and the most general solution is

$$\rho = \phi(\psi_1, \psi_2, \dots, \psi_{2n-1}) \quad \dots \quad (14)$$

in which ϕ is the most general function of the $(2n-1)$ variables.

§ 5. If the systems are not subject to external disturbance there is little more to be said. Of the $2n-1$ quantities $\psi_1, \psi_2, \dots, \psi_{2n-1}$, one (say ψ_1) may, without loss of generality, be taken to be identical with E ; the remaining $(2n-2)$ ψ 's are necessarily functions of quantities other than E . Thus it appears that although

$$\rho = \phi(E),$$

(the solution leading to equipartition of energy), is a particular solution of the general equations, it is by no means the only solution. In other words, equipartition, although possible, is not necessary. This is as it should be, for Maxwell's condition of continuity of path is not satisfied.

§ 6. Maxwell and Rayleigh now suppose that the system is subject to certain external agencies, and postulate that these agencies shall be such that by them each system is made to pass through all phases which are consistent with the conservation of energy. From the point of view of this paper, they postulate that the elements of fluid are moved out of their stream-lines, and this in such a way that every element is made to pass over the whole of the particular surface

$$E = \text{constant}$$

to which it initially belongs. If this postulate is granted their proof is unassailable, but they do not prove that the postulate is true in the case of any single system, and it seems to the present writer that for a large class of natural systems the postulate cannot possibly be true.

Consider, for instance, the case of a particle moving upon a horizontal plane, in which the disturbing influence is supplied by a system of rigid barriers. As a preliminary, suppose these barriers replaced by a continuous field of force, such that the potential becomes infinite over certain lines a, b, c, \dots in the plane. If this potential is included in the

energy-function E of § 4 the analysis of § 4 must hold, and the system moves only over a single stream-line, not over a complete energy surface. Now suppose the field of force to continuously change so that ultimately the potential is infinite over the lines $a, b, c \dots$, and is zero over the rest of the plane. This ultimate state is an exact mathematical representation of the case in which the motion is disturbed by rigid boundaries placed over the lines $a, b, c \dots$. However near the field of force may be to this ultimate state the argument of § 4 must be admitted to be valid. Hence *unless we assume the whole argument in some way to become invalid, when we finally pass to the limit*, it would seem that the theorem cannot possibly be true for the case in question. I cannot, for myself, see any reason for treating this limit as an exceptional case, and Lord Kelvin's recent experiments* seem to bear out this view.

§ 7. The same argument will, I think, apply to any case in which the motion is determined for all time by the state of the system at a given instant. For example, it applies if we try to replace our typical system by a mass of gas whether inclosed within rigid boundaries or not. When, however, the subsequent career of the system is in some way fortuitous the objection does not hold, and this class of exceptions includes the important case in which the systems are molecules of a gas, in which the disturbance of the path arises from fortuitous collisions with other molecules.

Application to Molecules of a Gas.

§ 8. Let us now suppose the exactly similar dynamical systems of § 2 to be the molecules of a gas.

Suppose that each molecule is surrounded by an imaginary sphere, and let it be supposed that these spheres are of such a radius that two molecules exert no action upon one another except when their spheres intersect. When two such spheres intersect an "encounter" is said to take place, lasting until the spheres again become clear of one another.

Binary Encounters.

§ 9. We shall begin by considering binary encounters only; that is to say, we assume that the event of a sphere being simultaneously intersected by two other spheres is so rare that it may be neglected.

We treat this case as follows:—As soon as an encounter

* Kelvin, Phil. Mag. [6] ii. p. 1.

begins between two molecules their existence as single molecules is supposed to be abruptly terminated, and their representative points are removed from our generalized space of $2n$ dimensions. During the progress of the encounter the two molecules together will be supposed to form a new dynamical system—a double molecule. This system will be specified by $4n$ independent coordinates, $2n$ for each constituent molecule. Hence any such system can be represented by a point in a space of $4n$ dimensions, one dimension corresponding to each coordinate. We shall not, however, require the whole of this $4n$ -dimensional space. If x, y, z, x', y', z' are the coordinates of the centres of the two molecules, the condition that an encounter is beginning or ending is

$$(x-x')^2 + (y-y')^2 + (z-z')^2 = 4R^2. \quad (15)$$

In the $4n$ -dimensional space this equation will be the equation of a certain "surface" S (of dimensions $4n-1$), and the representative points of all double molecules will be inside S . We shall find it convenient to denote each double molecule by *two* representative points, since the rôles of first and second molecule can be allotted in two different ways.

Let σ be the density in this new space, then the necessary and sufficient conditions for a steady state are

$$\frac{d\sigma}{dt} = 0, \quad (16)$$

$$\frac{d\rho}{dt} = 0, \quad (17)$$

in the latter of which the change in ρ includes that caused by the formation and dissolution of double molecules.

§ 10. Before determining the relation between ρ and σ we must make Boltzmann's assumption that the gas is in a "molekular-ungeordnet" state. Having made this assumption we proceed to calculate the number of encounters of a given kind which occur in an interval dt . Equating this to the number of representative points which cross the corresponding element of the surface S during the same interval we arrive at the equation

$$\sigma = \rho\rho', \quad (18)$$

in which σ is the density at any point on S , and ρ, ρ' the densities at the two points of $2n$ -dimensional space which are determined by the coordinates of the two encountering molecules.

The analysis of § 4 applies (with obvious modifications) to

the new space. Hence equation (16) may be replaced by the condition that σ shall be constant along a stream-line.

Let ρ, ρ' be the densities at points occupied by the representative points of the two component molecules, at the formation of a double molecule, and let $\bar{\rho}, \bar{\rho}'$ be the densities at the points representative of the same two molecules at the dissolution of the double molecule. Then $\rho\rho'$ and $\bar{\rho}\bar{\rho}'$ are the two values of σ at the two ends of a single stream-line in the $4n$ -dimensional space, and, therefore, by equation (18),

$$\rho\rho' = \bar{\rho}\bar{\rho}', \quad . \quad . \quad . \quad . \quad . \quad (19)$$

the same result as is obtained by Boltzmann's well-known H-theorem.

Since the motion is dynamically reversible we may take $\bar{\rho}, \bar{\rho}'$ to be the densities at formation, then ρ, ρ' will be the densities at dissolution, and the same result holds.

From this it follows that in equation (17) the decrease in ρ caused by the formation of double molecules of any specified kind is exactly counterbalanced by the increase caused by the dissolution of double molecules of the same kind. Hence in equation (17) $d\rho/dt$ may be taken to be the change in ρ caused solely by the continuous motion of the fluid, and may be treated as in § 4.

§ 11. To sum up, we have found that the equations of steady motion, on the hypothesis of binary encounters, may be expressed as follows:—

(α) Throughout the $2n$ -dimensional space, ρ must be constant along every stream-line.

(β) Throughout the $4n$ -dimensional space σ must be constant along every stream-line.

(γ) At every point on the boundary of the $4n$ -dimensional space we must have

$$\sigma = \rho\rho'.$$

To these may be added a fourth condition—

(δ) At every point on the boundary of the $2n$ -dimensional space (*i. e.* at infinity) the flow across the boundary must be nil, or what is the same thing, we must have

$$\rho = 0.$$

These conditions are necessary and sufficient for steady motion.

Ternary and Higher Encounters.

§ 12. By a simple extension of the method already explained the possibility of encounters of ternary and higher

orders may be considered. For instance, to take ternary encounters into account we imagine systems of triple molecules, these being represented in a space of $6n$ -dimensions. The density in this space being τ we have as conditions additional to those given in § 11—

(e) Throughout the $6n$ -dimensional space τ must be constant along every stream-line.

(f) At every point on the boundary of the $6n$ -dimensional space we must have

$$\tau = \rho \sigma.$$

§ 13. Encounters of higher orders may be similarly treated. If ρ_k is used to denote the density in the space of $2kn$ -dimensions, in which k -ple molecules are represented, the complete system of conditions for steady motion is

(i.) Along every stream-line in the $2kn$ -dimensional space,

$$\rho_k = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

(ii.) At every point on the boundary of the $2kn$ -dimensional space

$$\rho_k = \rho_a \rho_b, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

in which ρ_a, ρ_b refer to the two systems of molecules of orders a, b , of which the encounter results in the particular system of order k which is represented at the point in question (we therefore have always $a + b = k$).

If encounters of all orders are to be taken into account these conditions must be satisfied for all values of k from $k=1$ to $k=\infty$. In the case of $k=1$, equation (21) must be interpreted so as to become identical with the condition (δ) of § 11.

It will be noticed that if these conditions are satisfied for all values up to $k=\infty$, no hypothesis need be made as to the smallness of the radius of molecular action in comparison with the free path. The only assumption now made is that the gas is in a "molekular-ungeordnet" state.

Solution of Equations.

§ 14. Let χ be a quantity, a function of the coordinates of a molecule or system of molecules, such that throughout the undisturbed motion of the molecule or system χ maintains a constant value, and such that when two molecules or systems combine to form a new system the χ of the new system is equal to the sum of the χ 's of the component systems. Speaking loosely we may say that χ is defined as being capable of exchange between molecules at a collision but is indestructible.

Then a solution of our equations (20) and (21) will be seen to be

$$\log \rho_k = \chi (k=1, 2 \dots \infty). \quad \dots \quad (22)$$

Further, the difference between this value for $\log \rho_k$ and the most general solution for $\log \rho_k$ which is such as to satisfy equations (20) and (21) must be a quantity satisfying the conditions satisfied by χ . In other words, the most general solution of our equations consists of the superposition of solutions of the type of (22). Let $\chi_1, \chi_2, \chi_3, \dots \chi_s$ be independent quantities, each satisfying the conditions already postulated for χ , and let it be supposed that there are no other such quantities, then the most general solution of the equations of steady motion will be

$$\log \rho_k = A_1 \chi_1 + A_2 \chi_2 + \dots + A_s \chi_s,$$

in which $A_1 A_2 \dots A_s$ are independent and, so far, arbitrary constants.

§ 15. The quantities $A_1 A_2 \dots A_s$ can be uniquely determined from a knowledge of the values of $\Sigma \chi_1, \Sigma \chi_2, \dots$ the summation extending throughout the gas, and the various sums accordingly each remaining constant throughout the motion of the gas. Hence for a given mass of gas (the values of $\Sigma \chi_1, \Sigma \chi_2 \dots$ being given) there is a unique solution for a steady state, provided that a steady state is possible.

§ 16. Let us next examine what quantities satisfy the conditions assumed for χ . Firstly, if we take $\chi_1 = 1$ for a single molecule, $\chi_1 = 2$ for a double molecule, &c., we see that χ_1 satisfies the requisite conditions, and $\Sigma \chi$ is proportional to the total mass of gas. Again, if we take $\chi_2 = 2E$, where E is the total energy of the molecule or system of molecules (including, if necessary, the potential energy in an external field of force), we see that χ_2 satisfies these conditions. As other obvious instances we may suppose χ to represent the amounts of translational or rotational momentum. As a final instance we may consider imaginary molecules which are capable of carrying a charge of electricity, and we notice that the amount of this charge would be a possible value for χ .

For instance, if we have a number of electrically charged spheres each of mass m and capacity C , inclosed in a vessel of which the velocity is (u_0, v_0, w_0) , the solution will be found to be

$$\rho = A e^{-h \left[m \left\{ (u-u_0)^2 + (v-v_0)^2 + (w-w_0)^2 \right\} + \frac{1}{C} (Q-Q_0)^2 \right]},$$

in which Q_0 is the mean value of Q , the electric charge.

§ 17. The ideal gas of the kinetic theory may be supposed to be devoid of mass-velocity, both translational and rotational, and to be fully defined, in its steady state, by its density and temperature. For such a gas the only χ 's which can occur are the χ_1 and χ_2 of the last section, so that the solution is

$$\log \rho = A_1 \chi_1 + A_2 \chi_2.$$

Changing the constants this becomes

$$\rho = A e^{-2hE}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

in which A , h are determined *uniquely* by the values of the density and temperature.

For such a gas we have, therefore, proved that there is only one steady state, subject to the hypothesis that the gas is "molekular-ungeordnet," and this steady state is that given by the well-known Boltzmann law.

To arrive at this result we have found it necessary to suppose that there are only two invariable quantities—the mass and energy of the gas (corresponding to the two variables density and temperature). The result may break down for either of two reasons :

(i.) It may be that there is some third invariable quantity connected with the coordinates of the gas. If this is so, two samples of a gas having the same temperature and density will not in general possess the same physical properties. The uniformity of the experimental results obtained from different samples of gas, seems to supply an argument of overwhelming strength against supposing this to be the case.

(ii.) It may be that the two quantities ($\Sigma \chi_1$ and $\Sigma \chi_2$) which have been supposed to be invariable are not really so. This is certainly the case with the gases of nature, in which the aggregate energy of the molecules is subject to dissipation into the æther.

If we admit this latter objection it is at once obvious, on physical grounds, that no steady state is possible. Mathematically we are left with a solution in which ρ is proportional to χ_1 , and is therefore constant in the $2n$ -dimensional space. This solution fails because it does not give $\rho=0$ at infinity.

Conclusion.

§ 18. To sum up, we have seen that for a gas of which the molecules are of any kind whatever, the solution for the steady state is unique when a steady state is possible. We have found out how to determine this steady state when the structure of the molecules is completely known. For an

ideal gas, defined as one in which the aggregate mass and aggregate energy of the molecules remain constant throughout any possible natural motion, and which is such that the physical state of the gas is fully defined by its density and temperature, this steady state is given by the well-known Boltzmann law. These results depend upon the "molekular-ungeordnet" assumption, but are not limited by the hypothesis of binary encounters.

If the Boltzmann law does not give the steady state there must be some other variables besides the density and temperature, a knowledge of which is necessary to determine the physical properties of a sample of gas.

A gas in nature can never attain a steady state on account of the interaction between matter and æther. I have tried to follow out some of the consequences of this in former papers*.

In a future paper I hope to apply the methods of the present paper to some problems of dissociation and ionization.

LXVI. *The Electrical Conductivity of Metals and their Vapours.*

By the Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge†.

§ 1. *Introduction.*

IT is known that mercury vapour, even at very high temperatures, is a good insulator; a better one in fact than air under similar conditions‡. Liquid mercury, on the other hand, is of course a good conductor, like other metals. Let us try to form some idea of what the difference in conductivity between the liquid and the saturated vapour amounts to.

It is stated in the paper referred to that mercury vapour at atmospheric pressure, even at a yellow heat, allowed a much smaller current to pass than air under similar conditions. With air, contained in a tube 7×1 inches, into which the electrodes dipped, a current was observed which was measured by ten scale-divisions on a sensitive galvanometer, when an E.M.F. of 156 volts was applied. We may suppose that one scale-division represented a current of not more than 10^{-9} amperes, and that the mercury vapour gave only $\frac{1}{5}$ the current observed with air. Thus the current would be 2×10^{-9} amp.

* "The Distribution of Molecular Energy," Phil. Trans. excvi. p. 397; "The Mechanism of Radiation," Phil. Mag. [6] ii. p. 421; "The Theoretical Evolution of γ ," Phil. Mag. [6] ii. p. 638.

† Communicated by the Author.

‡ J. J. Thomson, Phil. Mag. [5] xxix. p. 364.