XL. The H theorem and Professor J. H. Jeans's Dynamical theory of gases

S.H. Burbury F.R.S.

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stress is dissipated within a finite time, contrary to what we should expect from theoretical considerations. At any rate, whether or not it is admitted that the breaks in the curves indicate that the elastic limit has been reached, it is certain that at these points a discontinuity occurs, the law on the one side being entirely different from that on the other side.

In conclusion I wish to thank Professor Trouton and Professor Porter for the kind interest they have shown in the work, and for the suggestions which have enabled me to surmount many of the difficulties which have arisen during the investigation.

XL. *The H Theorem and Professor J. H. Jeans's Dynamical Theory of Gases.* By S. H. BURBURY, F.R.S.*

1. **B**OLTZMANN'S H Theorem professes to prove that whenever the state of a gas is other than the normal state, $\frac{dH}{dt}$ is negative, and H is a minimum in the normal state.

H is the function $\iiint_{-\infty}^{+\infty} (f \log f - f) du dv dw$; $f du dv dw$ being

the number per unit of volume of molecules whose component velocities lie between u and $u+du$, v and $v+dv$, w and $w+dw$. In the normal state as usually understood, $f = Ae^{-hm(u^2+v^2+w^2)}$. As a consequence of the theorem, H, once minimum, remains minimum for ever, making the process irreversible. Then the objection was made that the

Theorem, proving $\frac{dH}{dt}$ to be necessarily negative, if not zero,

proves too much, because we have only to reverse all the velocities simultaneously, and the system will retrace its course with H increasing. The question is how to explain the paradox.

2. Professor J. H. Jeans, a very strong mathematician, has dealt with this question in his recent work on the Dynamical Theory of Gases. He gives (art. 11) a definition of the density, ν , of a gas at a point P: namely, ν is the number of molecules in a volume at P, which volume is very great compared with the mean molecular distance, but very small compared with the scale of variation of density of the gas. The definition is free from ambiguity. But it ignores variations of density on the scale of the intermolecular distances.

* Communicated by the Author.

There seems to be no reason why the density should vary at all on a scale infinitely larger than that of the intermolecular distances, unless in a field of external force such as gravity. Jeans's definition virtually assumes ν to be constant, except as varied by external forces.

3. He then gives the usual proof of the *H Theorem* on the hypothesis of "molecular chaos" (art. 15). This is the hypothesis which I call condition A, namely, that the chance of a molecule having velocities within assigned limits is independent of the positions of all the other molecules for the time being, and also independent of the velocities of all the other molecules for the time being, subject only to the constancy of $\frac{1}{2}\sum m(u^2 + v^2 + w^2)$, the total kinetic energy. The legitimacy of this assumption is, Jeans says, not self-evident, because it is conceivable, for instance, that molecules having nearly equal velocities should tend to flock together. He reserves the consideration of this question to later chapters.

4. In Chapter II. he introduces a new notation. Given a system of N molecules, he calls the $3N$ position coordinates $x_1 y_1 \dots z_N$, and the $3N$ component velocities $u_1 v_1 \dots w_N$, the "coordinates of a point in a generalized space of $6N$ dimensions." Every state of the system is represented by a point in that space, and the series of states which follow each other in natural motion are represented by a line in that space. This is a change in notation, advantageous it may be, but still only in notation. And as no new hypothesis is expressly introduced, the physical relations between the molecules must be understood to remain unaffected. Therefore every proposition concerning these relations, true in the usual notation, is true in the new notation, and *vice versa*. Also every proposition which can be proved by the use of the new notation, can be proved—I do not say proved equally well, but can be proved—by the use of the old notation. If the new method leads, or appears to lead, to any physical results not attainable by the ordinary method, that can only be because along with the new method we have introduced some new hypotheses unawares.

5. Jeans then discusses, arts. 39–54, the "Partition of the generalized space among the position coordinates." We are to suppose the three-dimension space Ω in which the molecules are moving to be divided into n equal cells $\omega_1 \omega_2 \dots \omega_n$, each of volume ω , so that $\Omega = n\omega$. The number of ways in which N molecules can be assigned to the n different cells, so that there shall be a_1 in ω_1 , a_2 in ω_2 , &c. with $a_1 + a_2 + \dots a_n = N$ is

$$\theta = \frac{N!}{a_1! a_2! \dots a_n!} \text{ (equation 60, p. 39).}$$

This means that the molecules are scattered at random through the space Ω . The most probable distribution is found by making θ maximum, and is when

$$\sum_{s=1}^{s=n} a_s \log a_s \text{ is minimum, that is when } a_1 = a_2 = \dots = a_n.$$

Subsequently (art. 55) he discusses the Partition of the generalized space as regards the velocities. This he says is to be effected in the same way as in the case of the position coordinates. That is, we are to suppose another three-dimension space, or diagram of velocities, and u, v, w are the coordinates in that diagram of points scattered at random through it, but they are to be subject to one new condition, namely, that $\sum m(u^2 + v^2 + w^2) = \text{constant}$ (equation 98). This new space, let us call it Ω' , may be divided into n equal cells, $\omega_1' \omega_2' \dots \omega_n'$, each of volume ω' , and the number of ways in which N molecules may be distributed through Ω' , so that there shall be f_1 in ω_1', f_2 in $\omega_2', \&c.$, with $\sum f = n$, is

$$\theta' = \frac{N!}{f_1! f_2! \dots f_n!}.$$

It is shown that θ' is maximum when

$$\iiint f \log f \, du \, dv \, dw \text{ is minimum.}$$

So the solution is given by making

$$\iiint f \log f \, du \, dv \, dw \text{ minimum,}$$

given

$$(1) \iiint f \, du \, dv \, dw = 1 \text{ (97), expressing only the fact that the number of molecules is constant ;}$$

$$(2) \iiint m(u^2 + v^2 + w^2) \, du \, dv \, dw = \text{constant (98).}$$

6. The usual method leads to

$$f = A e^{-hm(u^2 + v^2 + w^2)}, \text{ i. e. Maxwell's law.}$$

No mention has been made of any possible relation between velocities and space coordinates, such as that referred to by Jeans's art. 15. If any such existed it would manifestly vitiate the reasoning. It is therefore assumed by necessary implication (*a*) that no such relation exists, and therefore that the chance of a molecule having velocities within assigned limits is independent of the positions of all the other molecules for the time being. Further, it is expressly stated that the only relation existing among the

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velocities is (98). It is therefore assumed (*b*) that the chance of a molecule having velocities within assigned limits is, subject to (98), independent of *the velocities* of all the other molecules for the time being. Assumptions (*a*) and (*b*) together amount to Condition A, or "molecular chaos." Jeans has therefore by implication assumed Condition A. Maxwell's law distinctly asserts Condition A. If therefore you could prove Maxwell's law without expressly or by implication assuming Condition A, you would prove Condition A to be a physical fact, self-existent I suppose. But Jeans has proved Maxwell's law only on the implied assumption of Condition A. He has proved it, that is, on precisely the same assumption as all former writers have done. He has in no way altered the logical position of the Kinetic Theory of Gases.

7. With regard to the proof contained in arts. 39-54, Jeans proves, as I said, that θ is maximum when $a_1 = a_2 \dots = a_n$. And this he shows is equivalent to making ν constant on average. And further that, the a 's being very great, θ becomes infinitely less than its maximum when ν differs considerably from its constant or mean value, so that ν may be regarded as everywhere constant. I think that with infinitely small molecules and no forces acting, this follows from the definition of ν . Also, is not the result that all the a 's are equal when θ is maximum evident from the mere inspection of θ ? And then may we not write $a_s = \omega_s \nu_s$. And, therefore, $\nu_1 = \nu_2 \dots = \nu_n$?

8. The question occurred to me whether the number of possible arrangements of the molecules, which Jeans calculates, has any effect on the state of any physical system. Consider, for instance, a vertical column of gas under the earth's attraction. The number of ways in which the molecules can be assigned to equal elements of the column is immensely greater, according to Jeans's calculation of θ , when they are distributed with uniform density than when they are distributed according to any other law. Has this fact any influence on the actual distribution? I think none whatever, if the molecules are, as Jeans assumes (p. 39), infinitely small. I do not think Jeans would say that it has any. In Jeans's distribution the chance

of a given molecule being in the cell ω , is $\frac{\omega}{\Omega}$, and is independent of the position of the cell. We might say that equal cells have equal value for the purposes of the distribution. In the vertical column the chance of a given molecule being in the elementary cell ω is $\frac{\omega}{\Omega} e^{-2hgs}$, s being the height of the

cell above the base of the column. We might say that the value of a cell for the purposes of this distribution is proportional to e^{-2hgs} . On this principle we find that the density at height s is proportional to e^{-2hgs} as Boltzmann teaches, and is not affected in any way by Jeans's law of distribution.

9. In arts. 62-65 Jeans discusses the assumption of molecular chaos. The number of molecules whose space coordinates lie between x and $x + dx$, &c., and their velocities between u and $u + du$, &c., whatever be the positions and velocities of the other molecules, is denoted by v_p . It can evidently be written

$$v_p = N.f(u\ v\ w)\ du\ dv\ dw\ dx\ dy\ dz \iiint dx_b\ dx_c \dots dy_b\ dy_c \dots,$$

in which $x_b\ y_b\ z_b, x_c$, &c. denote the space coordinates of the molecules not included in v_p . Similarly the number whose position coordinates lie between $x' \dots x' + dx'$, &c., and their velocities between $u' \dots u' + du'$, &c., is given by

$$v_p = N.f(u'\ v'\ w')\ du'\ dv'\ dw'\ dx'\ dy'\ dz' \iiint dx_c \dots dy_c \dots dz_c,$$

$x_c\ y_c$, &c. now denoting the position coordinates of all the molecules except those which are included in v_p or v_q .

If $v = \iiint dx\ dy\ dz \iiint du\ dv\ dw$, over all the molecules, v includes all possible states of the system and means the same thing as the volume of Jeans's generalized space. And

$\frac{v_p}{v}, \frac{v_q}{v}$ represent respectively the chances of a molecule being included in v_p or in v_q .

The question is whether these chances are independent of each other. Now the motion being continuous, the velocities and positions of all the molecules at any instant are determinate functions of their velocities and positions at the initial instant t seconds ago. Consider two molecules m and m' ; let u_0 and u'_0 denote their initial velocities. If m and m' exert no forces on each other during the time t , and no third body sensibly influences both during the time t , and if $u\ u'$ were initially independent, then at the given instant u cannot be a function of u' . If $\phi(u)\ du$ be the chance of u lying between assigned limits, $\phi(u')\ du'$ the same for u' , it is certain that $\frac{d\phi(u)}{du'} = 0$. Similarly $\frac{d\phi(u')}{du} = 0$. $\phi(u)$ and $\phi(u')$ are then independent chances.

Clearly, then, if there be no intermolecular forces at all, the chances are independent. And they may be independent if t be small enough and the initial distance between m and

m' great enough. But if, during the time t , m and m' exert sensible forces on each other, it is certain that in general the two chances $\phi(u)$ and $\phi(u')$ are not independent. The question depends on the forces, and on nothing else whatever. It cannot be affected by any change in notation. There is indeed an attempted justification of the assumption of independence in the latter part of art. 65, p. 57. But it is only by reference to the analysis of Chapter III., the Partition of the generalized space, in which was assumed by necessary implication that molecular chaos or Condition A exists. It is impossible to prove a physical fact by merely using a new notation.

10. Jeans then, pp. 59, 60, gives an "Analysis of the *H* Theorem." He reminds us that to obtain strictly accurate results, the quantities he deals with must not be regarded as applying to a single system, but to the average of all systems satisfying certain conditions. These conditions I suppose are that each system consists of the same number N of similar molecules, and has the same mean kinetic energy. Then he assumes (art. 68) that the function $\bar{f}$ (art. 1 above) consists of two numerically equal parts, one half containing those molecules whose velocities are u, v, w , and the other half those whose velocities are $-u, -v, -w$. If one of these equal parts corresponds to a direct motion, the other corresponds to the reversed motion (art. 1 above). Whence it follows that, taking both motions into account, $\frac{dH}{dt}$ is on average as often positive as negative, is in fact on average zero.

11. This argument, it should be noted, does not affect the mathematical correctness of the *H* Theorem. The theorem is founded on a certain assumption, namely, that the number per unit of time of collisions between pairs of molecules, one from the class F , and other from the class f , the two molecules being so situated that after collision they are in the classes F' and f' respectively, is proportional to Ff , that is to the number of such pairs which exist—and is not generally proportional to $F'f'$. This assumption, though I deny its legitimacy, justifies, if true, the *H* Theorem. But if it applies to the direct, it cannot apply to the reversed motion, because the pairs of molecules which in the reversed motion pass from the classes F and f to the classes F' and f' , are the identical pairs which in the direct motion passed from F' and f' to F and f , and their number is therefore by the assumption proportional, not to Ff , but to $F'f'$. Therefore the *H* Theorem is inapplicable to the reversed motion by

failure of the assumption on which it is based. And the mathematical correctness of Boltzmann's theorem, granted his assumption, is preserved. The doubt is whether the assumption itself is valid.

12. It is proved *only in the normal state* that u, v, w are as likely to occur as $-u, -v, -w$. We have then, it may be said, no right to assume it in an analysis of the H Theorem, because that theorem deals only with systems in abnormal states. I understand, however, Jeans's meaning to be this. According to the H Theorem the system, given in an abnormal state, passes into the normal state. But *when it is normal*, u, v, w are as probable as $-u, -v, -w$, and therefore, the *motion being continuous*, the passage from the abnormal to the normal is just as frequent, and no more so, than the reverse. In this form the argument is good against Boltzmann as an *argumentum ad hominem*. But it makes the continuity of the motion a vital point. For if there be any the least discontinuity in the original motion, caused, say, by some external disturbance, it ceases to be true that the system, starting with velocities $-u, -v, -w$, will retrace the course of a system which ended with u, v, w . And therefore we cannot prove that on average of both motions $\frac{dH}{dt}$ is zero.

The discontinuity would be fatal to Jeans's argument, but not to the H Theorem.

13. I agree with Jeans that as a fact on average of all systems and of all time, $\frac{dH}{dt} = 0$, provided that the motion be continuous and protected from external disturbance. I agree with him also that, as a fact, on the average of all systems and all time, the states u, v, w , and $-u, -v, -w$ occur with equal frequency. I agree further with him that on average of all systems and all time H is nearly minimum. I expressed that myself in the form that when H differs little from its minimum, $\frac{dH}{dt}$ and $\frac{d^2H}{dt^2}$ are very small, whereas if

H differs much from its minimum $\frac{dH}{dt}$ may be very great.

For by consideration of the direct and reverse motions, we see that the number per unit of time of collisions by which two molecules pass from the classes F and f to the classes F' and f' , is proportional, not indeed necessarily to Ff as Boltzmann assumes, but either to Ff or else to $F'f'$, and as often to one as the other. But when H is nearly minimum $F'f' - Ff$ is in

general very small, and $(F'f' - Ff) \log \frac{Ff}{F'f'}$, of the second order of small quantities. But $\frac{dH}{dt}$ consists of terms either of this form or of the form $(Ff - F'f') \log \frac{Ff}{F'f'}$ and is therefore, whatever its sign, very small, and so is $\frac{d^2H}{dt^2}$.

It follows that any given system will remain for very long periods of time with *H* nearly minimum, though *H* may occasionally for short periods deviate into higher values. As for each system on average of time, so at each time on average of all systems, *H* is nearly minimum, which agrees with Jeans's conclusion.

Let us suppose there are *N* states in which $H = H_0$, and is minimum. Of these *N* states there are say n_1 states, each of which is the end of a course in which *H* has fallen from H_1 , its last maximum, to H_0 , and n_2 in which it has fallen from H_2 , its last maximum, to H_0 . And if $H_2 < H_1$, $n_2 > n_1$. Similarly for each of the *N* states there is a last maximum of *H*, and $N = n_1 + n_2 + \dots + n_N$. Then I should say $\frac{n_1}{N}$ measures the chance of *H* having the value H_1 , $\frac{n_2}{N}$ the chance of its having the value H_2 , and so on; and it may be that $\frac{n}{N}$ is infinitesimal for all values of *H* not infinitely near to H_0 . That gives Jeans's result.

14. If, however, there are in fact as many courses in which *H* passes from H_0 to H_1 , as in which it passes from H_1 to H_0 , it is not true that the variations of *H* constitute an irreversible process. It is not necessary to assume that the fall from a maximum H_1 to H_0 is always followed by a rise to precisely the same value H_1 as the next maximum, so that the system oscillates. It is sufficient to say, as we have said, that, on average of all systems and all time, motions in one direction happen as frequently as in the other direction.

15. Boltzmann's own explanation of our paradox was that the reversed motion, in which *H* increases, although possible, is in a very high degree less probable than the direct motion in which *H* diminishes, and on this he founded his doctrine of the connexion between reversibility and probability. I think this explanation cannot be reconciled with the theorem; for if Maxwell's law holds when *H* is minimum, which the theorem is supposed to prove, the state in which the velocities are typically $+u$, $+v$, and $+w$, and the state in which they are $-u$, $-v$, and $-w$ are equally probable

states. To assert that one is in a high degree more probable than the other, would be contrary to Maxwell's law.

16. The real defect in the H Theorem, and in every proof yet given of Maxwell's law, consists in my opinion in this, that it ignores the continuity of the motion altogether. The H Theorem is based wholly on the assumption mentioned in art. (11) above. Now let us suppose that at a given initial instant the state of the system is formed as follows:— One person assigns component velocities u, v, w to each molecule according to any law he pleases, subject only to the condition that $\Sigma m(u^2 + v^2 + w^2) = E$. And another person, to whom these assigned velocities are wholly unknown, scatters the molecules through the space Ω . In that case Condition A is satisfied at the initial instant, Boltzmann's assumption art. (11) above is satisfied, and if H is not minimum, $\frac{dH}{dt}$ is at that instant negative. But in the supposed distribution, the velocities are just as likely to have all the opposite values $-u -v -w$ as u, v, w . In either case at the initial instant $\frac{dH}{dt}$ is negative. If, however, the system were left to itself for a finite time, and then the final velocities were reversed, the system would retrace its course back to the initial state. And immediately before it arrives at that state $\frac{dH}{dt}$ is evidently positive. But when it has arrived at that state $\frac{dH}{dt}$ becomes discontinuously negative, because then the original velocities u, v, w would have become $-u -v -w$. And, as we have seen, $\frac{dH}{dt}$ is negative in that state as well as in the original state. $\frac{dH}{dt}$, if not zero, must be discontinuous when the system in its reversed course passes through its initial position.

17. That is the history of the initial state formed as I have supposed it to be formed. In dealing with the subsequent course of the system, to prove the H Theorem, or Maxwell's law, we assume, and if we are to prove the proposition we must assume, that the independence of the molecular velocities, or as I call it Condition A, exists at every instant during the motion. But if the motion be continuous, the state of the system at any instant is a determinate function of the initial state and of the time elapsed, and of

nothing else whatever. Now that the velocities of a set of molecules, being functions of the same set of initial variables and of the same time, should be always independent of each other, is, if it is to be taken as an exact statement, a mathematical impossibility. There must arise correlation between the velocities, at least of neighbouring molecules, as Jeans suggests in his art. 15.

18. In my unorthodox opinion therefore, neither Maxwell's law nor the *H Theorem* are true accurately, if the motion is continuous. As regards Maxwell's law, it may be for some important purposes accurate enough. If, for instance, we wish to calculate the theoretical value of the coefficient of diffusion between rare gases for comparison with experiment, approximate numerical results are all we require, and all we can have. And it may well be that Maxwell's law gives a sufficiently near approximation. This I have never denied. But in considering the question of reversibility, the method of approximation is ineffectual. For suppose two states of a gas, state A and state B. In state A the position and velocities of the molecules are denoted respectively by x, y, z and u, v, w . In state B they have nearly the same values as in A, and the differences are for some purposes negligible. Nevertheless these differences, however small, may in time cause the two systems to diverge widely from each other. One may be asymptotic, *H* continually approaching its minimum, the other may be cyclic. The asymptotic character cannot be established by any approximate reasoning.

19. If I am right in saying that Maxwell's law, founded as it is on the assumption of Condition A, and asserting as it does the truth of Condition A, cannot in continuous motion be accurately true, nevertheless the system started as I have supposed in art. 16 above and left to itself to move in continuous motion, must ultimately settle down into stationary motion of some kind, and must then have a normal state of some kind. If it be not Maxwell's law, what is it? I should answer the question thus—Firstly, in that normal state Condition A must not completely prevail. Secondly, the state in which the velocities of the N molecules are typically u, v, w , and the state in which they are typically $-u, -v, -w$, must in the stationary motion be equally probable. Both conditions are satisfied if "The chance of the N molecules having velocities within assigned limits is " $\Lambda e^{-hQ} du_1 \dots dw_N$, and
 $Q = \Sigma m(u^2 + v^2 + w^2) + \Sigma \Sigma b(uu' + vv' + ww')$,
 " where b is a function of r , the distance between the molecules

“ whose velocities are $u\ v\ w$ and $u'\ v'\ w'$, which is evanescent “ except for small values of r .” This does not satisfy Condition A. Also the second condition is evidently satisfied because Q is a quadratic function.

20. I suggested myself in ‘Nature,’ February 1895, in aid of the H Theorem, that no material system ever does remain for any considerable time in exactly continuous motion, free from external disturbances. Such disturbances are always happening, and their effect, if they come at haphazard without regard to the state of the system for the time being, is *pro tanto* to renew or to maintain the independence of the molecular motions, *i. e.* Condition A, and so to make H diminish. I think that is true. We may assume that if the disturbances are frequent enough and great enough,

$\frac{dH}{dt}$ will be in general negative or zero. But then we must remember that, as regards this disturbed system, it is not true that were all the velocities at any instant reversed the system would retrace its course, because the disturbances are not included in the reversal. I think therefore that the true explanation of the paradox of art. 1 above is as follows:--

The system either is or is not isolated, that is protected throughout the motion from all external disturbances. If we take the first hypothesis, that it is isolated, it is not true that the condition of independence (art. 17) exists. Therefore it is

not true that $\frac{dH}{dt}$ is necessarily negative. But it is true that

on reversal of the velocities the system would retrace its course. There is a reversed motion, but there is no H Theorem. If we take the second hypothesis, that disturbances are con-

tinually happening, it may be true that $\frac{dH}{dt}$ is generally

negative. But it is not true that on reversal of the velocities the system would retrace its course. There is an H Theorem, but there is no reversed motion. The reason why we obtain for the same system first one and then the other of two incon-

sistent results, first that $\frac{dH}{dt}$ is negative, secondly that $\frac{dH}{dt}$

is positive, is because we apply to the same system first one and then the other of two inconsistent hypotheses.