however, like those of chromic oxide and the oxide of zinc, in which a shifting of a region of maximum of reflecting-power towards the longer wave-lengths actually occurs when the pigment is heated.

It had been our purpose in the investigation just described to extend our spectro-photometric measurements to the very low temperatures obtainable by the use of solid carbon dioxide, but we have been compelled by lack of time to content ourselves with noting such changes as could be detected with the unaided eye. The change observed was in every case that which would be brought about by increase of reflecting-power. There was no increase in the saturation of the colour, rather, on the other hand, a paling or dilution of the tint, as though there were a tendency towards white. Houston*, who made a similar set of observations at the higher temperatures reached by the evaporation of carbon bisulphide or sulphurous acid, arrived at a similar result. Ackroyd, from theoretical considerations, concluded that as the absolute zero is approached the prevailing tints of pigments will be blues and violets, merging finally into white.

Ackroyd, Hartley, as also Houston and Thomson, and still earlier Schœnbein and Brewster, have had something to say concerning the explanation of these phenomena. Their various views need not be touched upon here, unless it be to call attention to the opening paragraph of Ackroyd's paper, which contains an important statement. Ackroyd says:—"These changes embrace a class of phenomena, quite as important in their way as phosphorescence and fluorescence, *with which in fact they are intimately connected.*" It is our opinion that the connexion is indeed a most intimate one, and that every change of colour that pigments undergo is to be regarded simply as a symptom of changes in the radiating-power of the substance.

Physical Laboratory of Cornell University,
June 1891.

LIII. *Dynamical Problems in Illustration of the Theory of Gases.* *By* Lord Rayleigh, *Sec. R.S.*†

Introduction.

THE investigations, of which a part is here presented, had their origin in a conviction that the present rather unsatisfactory position of the Theory of Gases is due in some

* *Loc. cit.* p. 123.

† Communicated by the Author.

degree to a want of preparation in the mind of readers, who are confronted suddenly with ideas and processes of no ordinary difficulty. For myself, at any rate, I may confess that I have found great advantage from a more gradual method of attack, in which effort is concentrated upon one obstacle at a time. In order to bring out fundamental statistical questions, unencumbered with other difficulties, the motion is here limited to one dimension, and in addition one set of impinging bodies is supposed to be very small relatively to the other. The simplification thus obtained in some directions allows interesting extensions to be made in others. Thus we shall be able to follow the whole process by which the steady state is attained, when heavy masses originally at rest are subjected to bombardment by projectiles fired upon them indifferently from both sides. The case of pendulums, or masses moored to fixed points by elastic attachments, is also considered, and the stationary state attained under a one-sided or a two-sided bombardment is directly calculated.

Collision Formulæ.

If u', v' be the velocities before collision, u, v after collision, of two masses P, Q, we have by the equation of energy

$$P(u'^2-u^2)+Q(v^2-v'^2)=0, \qquad (1)$$

and by the equation of momentum,

$$P(u'-u)+Q(v'-v)=0. \qquad (2)$$

From (1) and (2)

$$u'+u=v'+v, \qquad (3)$$

or, as it may be written,

$$u'-v'=v-u,$$

signifying that the relative velocity of the two masses is reversed by the collision. From (2) and (3),

$$\left.\begin{aligned}(P+Q)u'&=(P-Q)u+2Qv\\(P+Q)v'&=2Pu+(Q-P)v\end{aligned}\right\} \qquad (4)$$

As is evident from (1) and (2), we may in (4), if we please, interchange the dashed and undashed letters. Thus from the first of (4),

$$(P+Q)u=(P-Q)u'+2Qv',$$

or

$$u'=\frac{P+Q}{P-Q}u-\frac{2Q}{P-Q}v'$$

$$=u+\frac{2Q}{P-Q}(u-v'), \quad . \quad . \quad . \quad . \quad (5)$$

In the application which we are about to make, P will denote a relatively large mass, and Q will denote the relatively small mass of what for the sake of distinction we will call a projectile. All the projectiles are equal, and in the first instance will be supposed to move in the two directions with a given great velocity. After collision with a P the projectile rebounds and disappears from the field of view. Since in the present problem we have nothing to do with the velocity of rebound, it will be convenient to devote the undashed letter v to mean the given initial velocity of a projectile. Writing also q to denote the small ratio Q : P, we have

$$u'=u+\frac{2q}{1-q}(u-v). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If u and v be supposed positive, this represents the case of what we may call a favourable collision, in which the velocity of the heavy mass is increased. If the impact of the projectile be in the opposite direction, the velocity u'', which becomes u after the collision, is given by

$$u''=u+\frac{2q}{1-q}(u+v). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The symbol v thus denotes the velocity of a projectile without regard to sign, and (7) represents the result of an unfavourable collision.

Permanent State of Free Masses under Bombardment.

The first problem that we shall attack relates to the *ultimate* effect upon a mass P of the bombardment of projectiles striking with velocity v, and moving indifferently in the two directions. It is evident of course that the ultimate state of a particular mass is indefinite, and that a definite result can relate only to probability or statistics. The statistical method of expression being the more convenient, we will suppose that a very large number of masses are undergoing bombardment independently, and inquire what we are to expect as the ultimate distribution of velocity among them. If the number of masses for which the velocity lies between u and $u+du$ be denoted by $f(u)du$, the problem before us is the determination of the form of $f(u)$.

The number of masses, whose velocities lie between u and $u+du$, which undergo collision in a given small interval of time, is proportional in the first place to the number of the masses in question, that is to $f(u)\,du$, and in the second place to the relative velocity of the masses and of the projectiles. In all the cases which we shall have to consider v is greater than u, so that the chance of a favourable collision is always proportional to $v-u$, and that of an unfavourable collision to $v+u$. It is assumed that the chances of collision depend upon u in no other than the above specified ways. The number of masses whose velocities in a given small interval of time are passing, as the result of favourable collisions, from below u to above u, is thus proportional to

$$\int_{u'}^{u} f(w)\,.\,(v_1-w)\,dw, \quad . \quad . \quad . \quad . \quad . \quad (8)^*$$

where u' is defined by (6); and in like manner the number which pass in the same time from above u to below u, in consequence of unfavourable collisions, is

$$\int_{u}^{u''} f(w)\,.\,(v_1+w)dw, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

u'' being defined by (7). In the steady state as many must pass one way as the other, and hence the expressions (8) and (9) are to be equated. The result may be written in the form

$$v_1\left\{\int_{u'}^{u}-\int_{u}^{u''}\right\}f(w)dw=\int_{u'}^{u''}wf(w)\,dw. \quad . \quad . \quad (10)$$

Now, if q be small enough, one collision makes very little impression upon u; and the range of integration in (10) is narrow. We may therefore expand the function f by Taylor's theorem:—

$$f(w)=f(u)+(w-u)f'(u)+\tfrac{1}{2}(w-u)^2f''(u)+\ldots;$$

so that

$$\int f(w)dw=wf(u)+\tfrac{1}{2}(w-u)^2f'(u)+\tfrac{1}{6}(w-u)^3f''(u)+\ldots,$$

$$\left\{\int_{u'}^{u}-\int_{u}^{u''}\right\}f(w)dw=(2u-u'-u'')f(u)$$
$$-\tfrac{1}{2}\{(u'-u)^2+(u''-u)^2\}f'(u)+\ldots$$
$$=-\frac{4q}{1-q}uf(u)-\frac{4q^2}{(1-q)^2}(v^2+u^2)f'(u)+\text{cubes of } q. \quad (11)$$

* In the present problem $v_1=v$; but it will be convenient at this stage to maintain the distinction.

Also

$$\int wf(w)dw = \int\{(w-u)+u\}f(w)dw$$
$$= \tfrac{1}{2}(w-u)^2 f(u) + \tfrac{1}{3}(w-u)^3 f'(u) + \dots$$
$$+ uf(u)\{wf(u) + \tfrac{1}{2}(w-u)^2 f'(u) + \dots\};$$

so that

$$\int_{u'}^{u''} wf(w)dw = uf(u)\,.\,(u''-u')$$
$$+ \{\tfrac{1}{2}f(u) + \tfrac{1}{2}uf(u)\}\{(u''-u)^2-(u'-u)^2\} + \dots$$
$$= \frac{4qv}{1-q}uf(u) + \frac{8q^2uv}{(1-q)^2}\{f(u)+uf'(u)\} + \text{cubes of } q. \quad (12)$$

As far as q^2 inclusive (10) thus becomes

$$\frac{4qv_1}{1-q}uf(u) + \frac{4q^2v_1}{(1-q)^2}(v^2+u^2)f'(u)$$
$$+ \frac{4qv}{1-q}uf(u) + \frac{8q^2uv}{(1-q)^2}\{f(u)+uf'(u)\} = 0,$$

or

$$uf(u)\{(1-q)v_1 + (1+q)v\} + qf'(u)\{v_1v^2 + u^2(v_1+2v)\} = 0.$$

If $v_1 = v$, q disappears from the first term as it stands, and will do so in any case in the limit when it is made infinitely small. Moreover, in the second term u^2 is to be neglected in comparison with v^2. We thus obtain

$$uf(u)\{1+v/v_1\} + qv^2f'(u) = 0 \quad \dots \quad (13)$$

as the differential equation applicable to the determination of $f(u)$ when q is infinitely small. The integral is

$$qv^2 \log f(u) + \tfrac{1}{2}(1+v_1/v)u^2 = \text{constant},$$

or

$$f(u) = Ae^{-hu^2}, \quad \dots \dots \dots \quad (14)$$

where

$$h = \frac{1+v/v_1}{2qv^2}; \quad \dots \dots \dots \quad (15)$$

or, if $v_1 = v$,

$$h = 1/qv^2. \quad \dots \dots \dots \quad (16)$$

The ultimate distribution of velocities among the masses is thus a function of the energy of the projectiles and not otherwise of their common mass and velocity. The ultimate state is of course also independent of the number of the projectiles.

The form of f is that found by Maxwell. To estimate the mean value of u^2 we must divide

$$\int_{-\infty}^{+\infty} u^2 f(u)\,du \text{ by } \int_{-\infty}^{+\infty} f(u)\,du.$$

Now

$$\int u^2 e^{-u^2/qv^2} du = -\tfrac{1}{2}qv^2\{ue^{-u^2/qv^2} - \int e^{-u^2/qv^2} du\},$$

so that

$$\int_{-\infty}^{+\infty} u^2 e^{-u^2/qv^2} du = \tfrac{1}{2}qv^2 \int_{-\infty}^{+\infty} e^{-u^2/qv^2} du.$$

The ratio in question is thus $\frac{1}{2}qv^2$, showing that the mean kinetic energy of a mass is *one half* that of a projectile, deviating from the law of equal energies first (1845) laid down by Waterston. We must remember, however, that we have thus far supposed the velocities of the projectiles to be all equal.

The value of A in (14) may be determined as usual. If N be the whole (very great) number of masses to which the statistics relate,

$$\mathrm{N} = \int_{-\infty}^{+\infty} f(u)\,du = \mathrm{A}\int_{-\infty}^{+\infty} e^{-u^2/qv^2} du = \mathrm{A}v\sqrt{(\pi q)}\,;$$

so that

$$f(u)\,du = \frac{\mathrm{N}}{v\sqrt{(\pi q)}}\, e^{-u^2/qv^2}\, du. \quad . \quad . \quad . \quad (15')$$

If we were to suppose that the chances of a favourable or unfavourable collision were independent of the actual velocity of a mass, there would still be a stationary state defined by writing $v_1 = \infty$ in (15). Under these circumstances the mean energy would be twice as great as that calculated above.

It is easy to extend our result so as to apply to the case of projectiles whose velocities are distributed according to any given law $\mathrm{F}(v)$, of course upon the supposition that the projectiles of different velocities do not interfere with one another. We have merely to multiply by $\mathrm{F}(v)dv$ and to integrate between 0 and ∞. Thus from (13) we obtain

$$2uf(u)\int_0^{+\infty} v\mathrm{F}(v)\,dv + qf'(u)\int_0^{+\infty} v^3\mathrm{F}(v)\,dv = 0. \quad . \quad (17)$$

If $\mathrm{F}(v) = e^{-kv^2}$, we find

$$\int v^3 e^{-kv^2} dv = -\frac{1}{2k}\left\{v^2 e^{-kv^2} - \int e^{-kv^2} 2v\,dv\right\},$$

so that

$$\int_0^{+\infty} v^3 e^{-kv^2} dv = \frac{1}{k} \int_0^{+\infty} v e^{-kv^2} dv. \quad . \quad . \quad . \quad (18)$$

Our equation then becomes

$$2ku f(u) + q f'(u) = 0,$$

giving

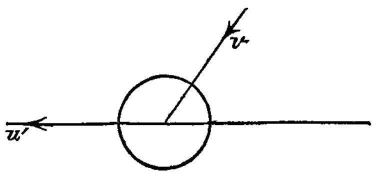
$$f(u) = \mathrm{A} e^{-ku^2/q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The mean energy of the masses is $\frac{1}{2}q/k$, and this is now *equal* to the mean energy of the projectiles. We see that if the mean energy of the projectiles is given, their efficiency is greater when the velocity is distributed according to the Maxwell law than when it is uniform, and that in the former case the Waterston relation is satisfied, as was to be expected from investigations in the theory of gases.

It may perhaps be objected that the law e^{-kv^2} is inconsistent with our assumption that v is always great in comparison with u. Certainly there will be a few projectiles for which the assumption is violated; but it is pretty evident that in the limit when q is small enough, the effect of these will become negligible. Even when the velocity of the projectiles is constant, the law e^{-u^2/qv^2} must not be applied to values of u comparable with v.

The independence of the stationary state of conditions, which at first sight would seem likely to have an influence, may be illustrated by supposing that the motion of the masses is constrained to take place along a straight line, but that the direction of motion of the projectiles, striking always centrically, is inclined to this line at a constant angle θ.

If u' be the velocity of the mass (unity) before impact,



and u after impact, B the impulsive action between the mass and the projectile,

$$u - u' = \mathrm{B} \cos\theta.$$

Also, if v, V be the velocities of the projectile (q) before and after impact,

$$q(v - \mathrm{V}) = \mathrm{B}\,;$$

so that

$$q(v-\mathrm{V})\cos\theta=u-u'.$$

By the equation of energy

$$u^2-u'^2=q(v^2-\mathrm{V}^2).$$

From these we find, as before,

$$u'=u-\frac{2q\cos^2\theta}{1-q\cos^2\theta}\left(u-\frac{v}{\cos\theta}\right).$$

This may be regarded as a generalization of (6); and we see that it may be derived from (6) by writing $v/\cos\theta$ for v, and $q\cos^2\theta$ for q. In applying equation (10) to determine the stationary state, we must remember that the velocity of retreat is now no longer w, but $w\cos\theta$, so that (10) becomes

$$v\left\{\int_{u'}^{u}-\int_{u}^{u''}\right\}f(w)dw=\int_{u'}^{u''}w\cos\theta f(w)dw.$$

The entire effect of the obliquity θ is thus represented by the substitution of $v/\cos\theta$ for v, and of $q\cos^2\theta$ for q, and since these leave qv^2 unaltered, the stationary state, determined by (15), is the same as if $\theta=0$.

The results that we have obtained depend entirely upon the assumption that the individual projectiles are fired at random, and without distinction between one direction and the other. The significance of this may be illustrated by tracing the effect of a restriction. If we suppose that the projectiles are despatched in pairs of closely following components, we should expect that the effect would be the same as of a doubling of the mass. If, again, the components of a pair were so projected as to strike almost at the same time upon opposite sides, while yet the direction of the first was at random, we should expect the whole effect to become evanescent. These anticipations are confirmed by calculation.

By (5) the velocity u_1', which on collision becomes u, is

$$u_1'=\frac{1+q}{1-q}u\mp\frac{2q}{1-q}v;$$

so that the velocity, which after *two* consecutive collisions upon the same side becomes u, is given by

$$u_2'=\frac{1+q}{1-q}u_1\mp\frac{2q}{1-q}v$$

$$=\frac{1+2q+(q^2)}{1-2q+(q^2)}u\mp\frac{4qv}{1-2q+(q^2)}.$$

The masses which by single collisions at velocity v would ultimately produce the same effect as these pairs are therefore very approximately $2q$.

If the projectiles be distributed in pairs in such a way that the components of each strike nearly simultaneously and upon *opposite* sides,

$$u_2' = \frac{1+q}{1-q}\left\{\frac{1+q}{1-q}u \pm \frac{2qv}{1-q}\right\} \mp \frac{2qv}{1-q}$$

$$= \frac{(1+q)^2}{(1-q)^2}u \pm \frac{4q^2v}{(1-q)^2}$$

$$= \frac{1+2q+(q^2)}{1-2q+(q^2)}u \pm \frac{4q\,.\,qv}{1-2q+(q^2)};$$

showing that the effect is the same as if the mass were doubled, and the velocity reduced from v to qv. Thus, when q is infinitely small, the effect is negligible in comparison with that obtained when the connexion of the components of a pair is dissolved, and each individual is projected at random.

Another Method of Investigation.

The method followed in the formation of equation (10) seems to lead most simply to the required determination of $f(u)$; but it is an instructive variation to consider directly the balance between the numbers of masses which change their velocities *from* and *to* u.

The number of masses whose velocities lie between u and $u+du$ being $f(u)du$, we have as the number whose velocities in a given small interval of time are expelled from the range du,

$$f(u)du(v-u) + f(u)\,du\,(v+u),$$

or

$$2vf(u)du.$$

This, in the steady state, is equal to the number which enter the range du from the two sides in consequence of favourable and unfavourable collisions; so that

$$f(u')(v-u')du' + f(u'')(v+u'')du'' - 2vf(u)du = 0\,. \qquad (20)$$

By (6), (7), since v is constant,

$$du' = \frac{1+q}{1-q}du, \quad du'' = \frac{1+q}{1-q}du\,;$$

so that

$$\frac{1+q}{1-q}f(u')\,.\,(v-u') + \frac{1+q}{1-q}f(u'')\,.\,(v+u'') - 2vf(u) = 0.$$

Now

$$v-u'=\frac{1+q}{1-q}(v-u),\ \ v+u''=\frac{1+q}{1-q}(v+u),$$

and thus

$$\frac{(1+q)^2}{(1-q)^2}\{(v-u)f(u')+(v+u)f(u'')\}-2vf(u)=0.$$

In this

$$f(u')=f(u)+\frac{2q(u-v)}{1-q}f'(u)+\frac{2q^2(u-v)^2}{(1-q)^2}f''(u)+\ \ldots$$

$$f(u'')=f(u)+\frac{2q(u+v)}{1-q}f'(u)+\frac{2q^2(u+v)^2}{(1-q)^2}f''(u)+\ \ldots;$$

so that

$$\frac{(1+q)^2}{(1-q)^2}\left\{2vf(u)+\frac{8qv}{1-q}uf'(u)+\frac{4q^2v^3}{(1-q)^2}f''(u)\right\}-2vf(u)=0,$$

or, when q is small enough,

$$8qv\{f(u)+uf'(u)\}+4q^2v^3f''(u)=0. \quad . \quad . \quad (21)$$

Accordingly

$$f(u)+uf'(u)+\tfrac{1}{2}qv^2f''(u)=0, \quad . \quad . \quad . \quad (22)$$

or on integration

$$uf(u)+\tfrac{1}{2}qv^2f'(u)=\mathrm{C}.$$

It is easy to recognize that the constant C of integration must vanish. On putting $u=0$, its value is seen to be

$$\mathrm{C}=\tfrac{1}{2}qv^2f'(0),$$

for $f(0)$ is not infinite. Now $f(u)$ is by its nature an even function of u, so that $f'(0)$ must vanish. We thus obtain the same equation (14) of the first order as by the former process.

Progress towards the Stationary State.

Passing from the consideration of the steady state, we will now suppose that the masses are initially at rest, and examine the manner in which they acquire velocity under the impact of the projectiles. In the very early stages of the process the momentum acquired during one collision is practically independent of the existing velocity (u) of a mass, and may be taken to be $\pm 2qv$. Moreover, the chance of a collision is at first sensibly independent of u. In the present investigation we are concerned not merely, as in considering the ultimate state, with the mass and velocity of a projectile, but also with the frequency of impact. We will denote by ν the whole number of projectiles launched in both directions in the unit of time in the path of each mass. The chance of a collision for a given mass in time dt is thus represented by $\nu\,dt$. The number of collisions by which masses are expelled from the range du in time dt is $f(u)du\,.\,\nu\,dt$. The number which enter the range from the two sides is

$$\{f(u-2qv)+f(u+2qv)\}du\,.\,\tfrac{1}{2}\nu\,dt,$$

so that the excess of the number which enter the range over the number which leave is

$$\{\tfrac{1}{2}f(u-2qv)+\tfrac{1}{2}f(u+2qv)-f(u)\}du\,.\,\nu\,dt,$$

and this is to be equated to $\frac{df(u,t)du}{dt}dt$. Thus

$$\frac{df}{\nu\,dt}=\tfrac{1}{2}f(u-2qv)+\tfrac{1}{2}f(u+2qv)-f(u)=2q^2v^2\frac{d^2f}{du^2}, \quad (23)$$

the well-known equation of the conduction of heat. When $t=0, f(u)$ is to be zero for all finite values of u. The Fourier solution, applicable under these conditions, is

$$f(u,t')=\frac{A}{\sqrt{t'}}e^{-u^2/4t'},$$

where t' is written for $2q^2v^2\nu t$. The total number of masses being N, we get to determine A

$$N=\int_{-\infty}^{+\infty}f(u,t')du=2\sqrt{\pi}\,.\,A\,;$$

so that

$$f(u,t')=\frac{N}{2\sqrt{(\pi t')}}e^{-u^2/4t'}. \quad . \quad . \quad . \quad . \quad (24)$$

If n be the whole number of collisions (for each mass), $n=\nu t$, and we have

$$4t'=4q^2v^2\,.\,2n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If the unit of velocity be so chosen that the momentum $(2qv)$ communicated at each impact is unity, (24) takes the form

$$f(u,n)=\frac{N}{\sqrt{(2\pi n)}}e^{-u^2/2n}, \quad . \quad . \quad . \quad . \quad (26)$$

which exhibits the distribution of momentum among the masses after n impacts. In this form the problem coincides with one formerly treated* relating to the composition of vibrations of arbitrary phases. It will be seen that there is a

* Phil. Mag. August 1880, p. 73

sharp contrast between the steady state and the early stages of the variable state. The latter depends upon the *momentum* of the projectiles, and upon the number of impacts; the former involves the *energy* of the projectiles, and is independent of the rapidity of the impacts.

The mean square of velocity after any number (n) of impacts is

$$N^{-1}\int_{-\infty}^{+\infty} u^2 f(u, n)du = n,$$

or, if we restore $4q^2v^2$,

$$\text{mean } u^2 = n \, . \, 4q^2v^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

It must be distinctly understood that the solution expressed by (24), (25), (26) applies only to the first stages of the bombardment, beginning with the masses at rest. If the same state of things continued, the motion of the masses would increase without limit. But as time goes on, two causes intervene to prevent the accumulation of motion. When the velocity of the masses becomes sensible, the chance of an unfavourable collision increases at the expense of the favourable collisions, and this consideration alone would prevent the unlimited accumulation of motion, and lead to the ultimate establishment of a steady state. But another cause is also at work in the same direction, and, as may be seen from the argument which leads to (13), with equal efficiency. The favourable collisions, even when they occur, produce less effect than the unfavourable ones, as is shown by (6) and (7).

We will now investigate the general equation, applicable not merely to the initial and final, but to all stages of the acquirement of motion. As in (20), (23) we have

$$\frac{df(u,t)du}{dt}dt = \frac{vdt}{v}\{\tfrac{1}{2}f(u') \, . \, (v-u')du' + \tfrac{1}{2}f(u'') \, . \, (v+u'')du'' - f(u) \, . \, v \, du\};$$

and thus by the same process as for (22)

$$\frac{df}{\nu \, dt} = 4q\frac{d}{du}\{uf(u)\} + 2q^2v^2\frac{d^2f}{du^2}. \quad . \quad . \quad . \quad (28)$$

If we write, as before,

$$t' = 2q^2v^2\nu t, \text{ and } h = 1/qv^2, \quad . \quad . \quad . \quad . \quad (29)$$

we have

$$\frac{df}{dt'} = \frac{d^2f}{du^2} + 2h\frac{d}{du}(uf). \quad . \quad . \quad . \quad . \quad (30)$$

2 G 2

Both in the case where the left side was omitted, and also when h vanished, we found that the solution was of the form

$$f = \sqrt{\phi} \, . \, e^{-\phi u^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where ϕ was constant, or a function of t' only. We shall find that the same form applies also to the more general solution. The factor $\sqrt{\phi}$ is evidently necessary in order to make $\int_{-\infty}^{+\infty} f(u)\, du$ independent of the time. By differentiation of (31),

$$\frac{df}{dt'} = \tfrac{1}{2}\phi_{-\frac{1}{2}} e^{-\phi u^2}(1 - 2\phi u^2)\frac{d\phi}{dt'},$$

$$\frac{d^2 f}{du^2} = -2\phi^{\frac{3}{2}} e^{-\phi u^2}(1 - 2\phi u^2),$$

$$u\frac{df}{du} + f = \phi^{\frac{1}{2}} e^{-\phi u^2}(1 - 2\phi u^2)\ ;$$

so that (30) is satisfied provided ϕ is so chosen as a function of t' that

$$\tfrac{1}{2}\phi^{-\frac{1}{2}}\frac{d\phi}{dt'} = -2\phi^{\frac{3}{2}} + 2h\phi^{\frac{1}{2}},$$

or

$$\frac{1}{4\phi^2}\frac{d\phi}{dt'} = -1 + \frac{h}{\phi}.$$

Thus

$$4t' = \int \frac{d\phi^{-1}}{1 - h\phi^{-1}} = -\frac{1}{h}\log(1 - h\phi^{-1}) + \text{const.},$$

where, however, the constant must vanish, since $\phi = \infty$ corresponds to $t' = 0$. Accordingly

$$\phi = \frac{h}{1 - e^{-4ht'}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

which with (31) completes the solution.

If t' is small, (32) gives $\phi = 1/4t'$, in agreement with (24); while if t' be great, we have $\phi = h = 1/qv^2$, as in (15′).

The above solution is adapted to the case where $f(u) = 0$ for all finite values of u, when $t' = 0$. The next step in the process of generalization will be to obtain a solution applicable to the initial concentration of $f(u)$, no longer merely at zero, but at any arbitrary value of u; that is, to the case where initially all the masses are moving with one constant velocity α.

Assume

$$f=\sqrt{\phi}\,.\,e^{-\phi(u-\psi)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where ϕ, ψ are functions of t' only. Substituting. as before, in (30), we find

$$\{1-2\phi(u-\psi)^2\}\left\{\tfrac{1}{2}\frac{d\phi}{dt'}+2\phi^2-2h\phi\right\}$$

$$+2\phi^2(u-\psi)\left\{\frac{d\psi}{dt}+2h\psi\right\}=0\,;$$

so that the equation is satisfied provided

$$\tfrac{1}{2}\frac{d\phi}{dt'}+2\phi^2-2h\phi=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and

$$\frac{d\psi}{dt'}+2h\psi=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The first is the same equation as we found before, and its solution is given by (32); while (35) gives

$$\psi=\alpha e^{-2ht'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Thus (32), (33), (36) constitute the complete solution of the problem proposed, and show how the initial concentration at $u=\alpha$ passes gradually into the steady state when $t'=\infty$. In the early stages of the process.

$$f(u,t')=\frac{1}{\sqrt{(4t')}}\,e^{-(u-\alpha)^2/4t'}\,; \quad . \quad . \quad . \quad . \quad . \quad (37)$$

to which the factor $\mathrm{N}/\sqrt{\pi}$ may be applied, when it is desired to represent that the whole number of masses is N. It appears that during the whole process the law of distribution is in a sense maintained, the only changes being in the value of u round which the grouping takes place, and in the degree of concentration about that value.

There will now be no difficulty in framing the expression applicable to an arbitrary initial distribution of velocity among the masses. For this purpose we need only multiply (33) by $\chi(\alpha)\,d\alpha$, and integrate over the necessary range. Thus

$$f(u,t')=\sqrt{\phi}\,.\int_{-\infty}^{+\infty}d\alpha\,\chi(\alpha)\;\mathrm{E}xp\{-\phi(u-\alpha e^{-2ht'})^2\}, \quad . \quad (38)$$

ϕ being given, as usual, by (32). The limits for α are taken $\pm\infty$; but we must not forget that the restriction upon the magnitude of u requires that $\chi(u)$ shall be sensible only for values of u small in comparison with v.

When is small, we have from (38),

$$f(u,t')=\frac{1}{\sqrt{(4t')}}\int_{-\infty}^{+\infty}d\alpha\,\chi(\alpha)\,e^{-(u-\alpha)^2/4t'}=\sqrt{\pi}\,.\,\chi(u)\text{ ultimately;}$$

so that

$$\chi(\alpha)=\frac{1}{\sqrt{\pi}}f(\alpha,0).$$

Accordingly the required solution expressing the distribution of velocity at t' in terms of that which obtains when $t'=0$, is

$$f(u,t')=\sqrt{\frac{\phi}{\pi}}\cdot\int_{-\infty}^{+\infty}d\alpha\,f(\alpha,0)\,\mathrm{Exp}\{-\phi(u-\alpha e^{-2ht'})^2\}\,.\,.\,(39)$$

We may verify this by supposing that $f(u,0)=e^{-hu^2}$, representing the steady state. The integration of (39) then shows that

$$f(u,t')=e^{-hu^2},$$

as of course should be.

An example of more interest is obtained by supposing that initially

$$f(u,0)=e^{-h'u^2};\quad .\ .\ .\ .\ .\ .\ .\ (40)$$

that is, that the velocities are in the state which would be a steady state under the action of projectiles moving with an energy different from the actual energy. In this case we find from (32), (39),

$$f(u,t')=\sqrt{\left(\frac{\phi}{\phi-h+h'}\right)}\,e^{-\frac{\phi h'u^2}{\phi-h+h'}}.\quad .\ .\ (41)$$

We will now introduce the consideration of variable velocity of projectiles into the problem of the progressive state. In (28) we must regard ν as a function of v. If we use $\nu\,dv$ to denote the number of projectiles launched in unit of time with velocities included between v and $v+dv$, (28) may be written

$$\frac{df}{dt}=4q\int\nu\,dv\,.\,\frac{d}{du}\{uf(u)\}+2q^2\int\nu\,v^2\,dv\,.\,\frac{d^2f}{du^2},\quad .\ (42)$$

which is of the same form as before. The only difference is that we now have in place of (29),

$$t'=2q^2t\int\nu\,v^2\,dv,\quad .\ .\ .\ .\ .\ .\ .\ (43)$$

$$h=\int\nu\,dv\div q\int\nu\,v^2\,dv.\quad .\ .\ .\ .\ (44)$$

In applying these results to particular problems, there is an important distinction to be observed. By definition $\nu\,dv$ represents the number of projectiles which in the unit *time* pass a given place with velocities included within the prescribed range. It will therefore not represent the distribution of velocities in a given *space*; for the projectiles, passing in unit time, which move with the higher velocities cover correspondingly greater spaces. If therefore we wish to investigate the effect of a Maxwellian distribution of velocities among the projectiles, we are to take, not $\nu = \mathrm{B}e^{-kv^2}$, but

$$\nu = \mathrm{B}\, v\, e^{-kv^2}. \qquad (45)$$

In this case, by (18),

$$h = k/q\,; \qquad (46)$$

and, as we saw, the mean energy of a mass in the steady state is equal to the mean energy of the projectiles which at any moment of time occupy a given space. From (43),

$$t' = \mathrm{B}q^2k^{-2}t. \qquad (47)$$

Pendulums in place of Free Masses.

We will now introduce a new element into the question by supposing that the masses are no longer free to wander indefinitely, but are moored to fixed points by similar elastic attachments. And for the moment we will assume that the stationary state is such that no change would occur in it were the bombardment at any time suspended. To satisfy this condition it is requisite that the phases of vibrations of a given amplitude should have a certain distribution, dependent upon the law of force. For example, in the simplest case of a force proportional to displacement, where the velocity u is connected with the amplitude (of velocity) r and with the phase θ by the relation $u = r\cos\theta$, the distribution must be uniform with respect to θ, so that the number of vibrations in phases between θ and $\theta + d\theta$ must be $d\theta/2\pi$ of the whole number whose amplitude is r. Thus if r be given, the proportional number with velocities between u and $u + du$ is

$$\frac{du}{2\pi\sqrt{(r^2 - u^2)}}. \qquad (48)$$

And, in general, if r be some quantity by which the amplitude is measured, the proportional number will be of the form

$$\phi(r, u)\, du, \qquad (49)$$

where ϕ is a determinate function of r and u, dependent upon the law of vibration. If now $\chi(r)\, dr$ denote the number of vibrations for which r lies between r and $r + dr$, we have altogether for the distribution of velocities u,

$$f(u) = \int \chi(r)\, \phi(r, u)\, dr. \qquad (50)$$

If the vibrators were left to themselves, $\chi(r)$ might be chosen arbitrarily, and yet the distribution of velocity, denoted by $f(u)$, would be permanent. But if the vibrators are subject to bombardment, $f(u)$ cannot be permanent, unless it be of the form already determined. The problem of the permanent state may thus be considered to be the determination of $\chi(r)$ in (50), so as to make $f(u)$ equal to e^{-hu^2}.

We will now limit ourselves to a law of force proportional to displacement, so that the vibrations are isochronous; and examine what must be the form of $\chi(r)$ in (8) in order that the requirements of the case may be satisfied.

By (15′), if N be the whole number of vibrators,

$$\frac{N\sqrt{h}}{\sqrt{\pi}}e^{-hu^2}=\int_u^\infty \frac{\chi(r)\,dr}{2\pi\sqrt{(r^2-u^2)}}. \quad . \quad . \quad . \quad (51)$$

The determination of the form of χ is analogous to a well-known investigation in the theory of gases. We assume

$$\chi(r)=Ar\,e^{-hr^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

where A is a constant to be determined. To integrate the right-hand member of (51), we write

$$r^2=u^2+\eta^2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

so that

$$\int_u^\infty \frac{\chi(r)\,dr}{\sqrt{(r^2-u^2)}}=A\int_0^\infty e^{-h(u^2+\eta^2)}\,d\eta=\frac{A\sqrt{\pi}}{2\sqrt{h}}e^{-hu^2}.$$

Thus

$$A=4hN. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

The distribution of the amplitudes (of velocity) is therefore such that the number of amplitudes between r and $r+dr$ is

$$N\,.\,4hr\,e^{-hr^2}\,dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

while for each amplitude the phases are uniformly distributed round the complete cycle.

The argument in the preceding paragraphs depends upon the assumption that a steady state exists, which would not be disturbed by a suspension, or relaxation, of the bombardment. Now this is a point which demands closer examination; because it is conceivable that there may be a steady state, permanent so long as the bombardment itself is steady, but liable to alteration when the rate of bombardment is increased or diminished. And in this case we could not argue, as before, that the distribution must be uniform with respect to θ.

If x denote the displacement of a vibrator at time t,

$$x=n^{-1}\,r\sin(nt-\theta), \quad dx/dt=r\cos(nt-\theta).$$

When $t=0$,

$$x=-n^{-1}r\sin\theta,\quad dx/dt=u=r\cos\theta\,;$$

and we may regard the amplitude and phase of the vibrator as determined by u, η, where

$$u=r\cos\theta,\quad \eta=r\sin\theta.$$

Any distribution of amplitudes and phases may thus be expressed by $f(u,\eta)\,du\,d\eta$.

If we consider the effect of the collisions which may occur at $t=0$, we see that u is altered according to the laws already laid down, while η *remains unchanged.* The condition that the distribution remains undisturbed by the collisions is, as before, that, for every constant η, $f(u,\eta)$ should be of the form e^{-hu^2}, or, as we may write it,

$$f(u,\eta)=\chi(\eta)\,e^{-hu^2}.$$

But this condition is not sufficient to secure a stationary state, because, even in the absence of collisions, a variation would occur, unless $f(u,\eta)$ were a function of r, independent of θ. Both conditions are satisfied, if $\chi(\eta)=\mathrm{A}\,e^{-h\eta^2}$, where A is a constant; so that

$$f(u,\eta)\,du\,d\eta=\mathrm{A}\,e^{-h(u^2+\eta^2)}\,du\,d\eta=2\pi\mathrm{A}\,e^{-hr^2}\,r\,dr.$$

Under this law of distribution there is no change either from the progress of the vibrations themselves, or as the result of collisions.

The principle that the distribution of velocities in the stationary state is the same as if the masses were free is of great importance, and leads to results that may at first appear strange. Thus the mean kinetic energies of the masses is the same in the two cases, although in the one case there is an accompaniment of potential energy, while in the other there is none. But it is to be observed that nothing is here said as to the rate of progress towards the stationary condition when, for instance, the masses start from rest; and the fact that the ultimate distribution of velocities should be independent of the potential energy is perhaps no more difficult to admit than its independence of the number of projectiles which strike in a given time. One difference may, however, be alluded to in passing. In the case of the vibrators it is necessary to suppose that the collisions are instantaneous; while the result for the free masses is independent of such a limitation.

The simplicity of f in the stationary state has its origin in the independence of θ. It is not difficult to prove that this law of independence fails during the development of the vibrations from a state of rest under a vigorous bombardment. The investigation of this matter is accordingly more complicated than in the case of the free masses, and I do not propose here to enter upon it.

In a modification of the original problem of some interest even the stationary distribution is not entirely independent of phase. I refer to the case where the bombardment is from one side only, or (more generally) is less vigorous on one side than on the other. It is easy to see that a one-sided bombardment would of necessity disturb a uniform distribution of phase, even if it were already established. The permanent state is accordingly one of unequal phase-distribution, and is not, as for the symmetrical bombardment, independent of the vigour with which the bombardment is conducted.

But in one important particular case the simplicity of the symmetrical bombardment is recovered. For if the number of projectiles striking in a given time be sufficiently reduced, the stationary condition must ultimately become one of uniform phase-distribution.

Under this limitation it is easy to see what the stationary state must be. Since the ultimate distribution is uniform with respect to phase, it must be the same from whichever side the bombardment comes. Under these circumstances it could not be altered if the bombardment proceeded indifferently from both sides, which is the case already investigated. We conclude that, *provided the bombardment be very feeble*, there is a definite stationary condition, independent both of the amount of the bombardment and of its distribution between the two directions. It is of course understood that from whichever side a projectile be fired, the moment of firing is absolutely without relation to the phase of the vibrator which it is to strike.

The problem of the one-sided bombardment may also be attacked by a direct calculation of the distribution of amplitude in the stationary condition. The first step is to estimate the effect upon the amplitude of a given collision. From (6), if u' be the velocity before collision, and u after,

$$u=u'+\frac{2q}{1+q}\,(v-u').$$

The fraction $2q/(1+q)$ occurs as a whole, and we might retain it throughout. But inasmuch as in the final result only one power of q need be retained, it will conduce to brevity to omit the denominator at once, and take simply

$$u=u'+2q(v-u'). \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

Thus if ρ, ϕ and r, θ be the amplitude and phase before and after collision respectively,

$$\left.\begin{array}{l} r\cos\theta=\rho\cos\phi+2q(v-\rho\cos\phi), \\ r\sin\theta=\rho\sin\phi\,; \end{array}\right\} \quad . \quad . \quad (57)$$

so that

$$r^2=\rho^2+4q\rho\cos\phi\ (v-\rho\cos\phi)+4q^2(v-\rho\cos\phi)^2.$$

From this we require the approximate value of ρ in terms of r and ϕ. The term in q^2 cannot be altogether neglected, but it need only be retained when multiplied by v^2. The result is

$$\rho=r-\delta r,$$

where

$$\delta r=2q(v\cos\phi-r\cos^2\phi)+\frac{2q^2v^2}{r}\sin^2\phi. \quad . \quad (58)$$

This equation determines for a given ϕ the value of ρ which the blow converts into r. Values of ρ nearer to r will be projected across that value. The chance of a collision at ρ, ϕ is proportional to $(v-\rho\cos\phi)$. Thus if a number of vibrators in state ρ, ϕ be $F(\rho)\,d\rho\,d\phi$*, the condition for the stationary state is

$$\int_0^{2\pi}d\phi\int_\rho^r(v-\rho\cos\theta)\,F(\rho)\,d\rho=0, \quad . \quad . \quad . \quad (59)$$

the integral on the left expressing the whole number (estimated algebraically) of amplitudes which in a small interval of time pass outwards through the value r.

By expansion of $F(\rho)$ in the series

$$F(\rho)=F(r)+F'(r)(\rho-r)+\dots,$$

we find

$$\int_\rho^r F(\rho)\,d\rho=F(r)\,\delta r-\tfrac{1}{2}F'(r)\,(\delta r)^2+\text{ cubes of }q,$$

$$\int_\rho^r \rho\,F(\rho)\,d\rho=r\,F(r)\,\delta r-\tfrac{1}{2}(\delta r)^2\{F(r)+rF'(r)\}+\text{cubes of }q.$$

* We here assume that the bombardment is feeble.

Again from (58),

$$\ldots \quad \int_0^{2\pi} \delta r \, d\phi = -qr + q^2v^2/r,$$

$$\int_0^{2\pi} \cos\phi \, \delta r \, d\phi = qv,$$

$$\int_0^{2\pi} (\delta r)^2 \, d\phi = 2q^2v^2,$$

$$\int_0^{2\pi} \cos\phi \, (\delta r)^2 \, d\phi = 0.$$

The condition for the stationary state is therefore

$$v\{\mathrm{F}(r)(-qr + q^2v^2/r) - \mathrm{F}'(r)\, q^2v^2\} - r\,\mathrm{F}(r)\, qv = 0,$$

or

$$\mathrm{F}(r)\{-2r + qv^2/r\} - \mathrm{F}'(r)\, qv^2 = 0.$$

Thus, on integration,

$$r^2 - qv^2 \log r + qv^2 \log \mathrm{F}(r) = \text{const.}, \quad . \quad . \quad (60)$$

or

$$\mathrm{F}(r) = \mathrm{A}r\, e^{-r^2/qv^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

The mean value of r^2, expressed by

$$\int_0^\infty r^3 \mathrm{F}(r)\, dr \div \int_0^\infty r\,\mathrm{F}(r)\, dr,$$

is qv^2; that is, the mean value of the maximum kinetic energy attained during the vibration is equal to the kinetic energy of a projectile. The mean of all the actual kinetic energies of the vibrators is the half of this; but would rise to equality with the mean energy of the projectiles, if the velocities of the latter, instead of being uniform, as above supposed, were distributed according to the Maxwellian law.

If we are content to assume the *law* of distribution, $\rho\, e^{-h\rho^2}$, leaving only the constant h to be determined, the investigation may be much simplified. Thus from (57) the gain of energy from the collision is

$$\tfrac{1}{2} r^2 - \tfrac{1}{2}\rho^2 = 2q\rho\cos\phi\,(v - \rho\cos\phi) + 2q^2v^2.$$

The chance of the collision in question is proportional to the relative velocity $(v-\rho\cos\phi)$; and in the stationary state the whole gain of energy is zero. Hence

$$\iint \rho\, e^{-h\rho^2}\, d\rho\, d\phi \{2q\rho\cos\phi\,(v-\rho\cos\phi)^2+2q^2v^3\}=0.$$

In the integration with respect to ϕ the odd powers of $\cos\phi$ vanish. Hence

$$2qv\int_0^\infty \rho\, d\rho\, e^{-h\rho^2}(qv^2-\rho^2)=0\,;$$

so that

$$h=1/qv^2,$$

as in (61).

Terling Place, Witham,
August 19, 1891.

LIV. *On the Discharge of Electricity through Exhausted Tubes without Electrodes. By* J. J. Thomson, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge.*

[Continued from p. 336.]

Phosphorescence produced by the Discharge.

THE discharge without electrodes produces a very vivid phosphorescence in the glass of the vessel in which the discharge takes place; the phosphorescence is green when the bulb is made of German glass, blue when it is made of lead glass. Not only does the bulb itself phosphoresce, but a piece of ordinary glass tubing held outside the bulb and about a foot from it phosphoresces brightly; while uranium glass will phosphoresce at a distance of several feet from the discharge. Similar effects, but to a smaller extent, are produced by the ordinary spark between the poles of an electrical machine.

The vessel in which the discharge takes place may be regarded as the secondary of an induction-coil, and the discharge in it shows similar properties to those exhibited by currents in a metallic secondary. Thus no discharge is produced unless there is a free way all round the tube; the discharge is stopped if the tube is fused up at any point. In order that the discharge may take place, it is necessary that the molecules of the gas shall be able to form a closed chain without the interposition of any non-conducting substance; indeed the discharge seems to be hindered by the