An Extension of Boltzmann's Minimum Theorem. By S. H. BURBURY, M.A., F.R.S. Received May 31st, 1895. Communicated June 13th, 1895, by G. H. BRYAN, F.R.S.

1. Let $f(p_1 \dots q_n)\,dp_1 \dots dq_n$, or shortly $f\,.\,dp_1 \dots dq_n$, denote the chance that a molecule of a gas shall at any instant have its n coordinates $p_1 \dots p_n$, and corresponding momenta $q_1 \dots q_n$ between the limits p_1, $p_1 + dp_1$, &c.

Similarly, let $F\,.\,dP_1 \dots dQ_n$ be the corresponding chance for the values $P_1 \dots P_1 + dP_1$ of the coordinates and momenta.

2. If at a given instant the variables $p_1 \dots Q_n$ stand to one another in a certain relation, an encounter between the two molecules ensues, that is, within a very short time after the given instant the variables $p_1 \dots Q_n$ will, by the mutual action of the two molecules alone, assume new values *conservatis conservandis*, which may be denoted by accented letters $p_1' \dots Q_n'$.

If we ask what is the number per unit of volume of pairs for which at this instant the variables are so related to one another, the answer usually given is that it is proportional to $Ff\,.\,dp_1 \dots dQ_n$. In other words, it is usual to assume the chances f and F to be independent.

3. On this assumption of independence, and on this assumption only, it has been proved that, if

$$H = \iiint \dots f(\log f - 1)\,dp_1 \dots dq_n,$$

$\frac{dH}{dt}$ is necessarily negative. If, therefore, when the system is isolated, F and f continue to be independent, $\frac{dH}{dt}$ continues to be negative. H tends to a minimum, which it reaches when the distribution of momenta is according to the Boltzmann-Maxwell law.

4. Now, systems may exist in which that independence of f and F for encountering molecules cannot be conceded. I have myself propounded the doctrine that the independence of f and F is only a

consequence of the (generally) assumed rarity of the medium, and that they cease to be independent as the medium becomes denser, on the ground that in the dense medium the proximity of two molecules, implied by their encounter, affords a presumption that they have recently been exposed to the same influences, and have acquired some velocities in common. However this may be, and I am not now assuming the truth of it, it is worth while to consider whether and how we can prove the theorem without assuming the independence of f and F. I propose in this paper to treat only the simplest case, regarding the molecules as equal elastic spheres.

5. Let c be the diameter of a sphere. Consider two spheres A and B. Let R be their relative velocity. About O, the centre of A, suppose a circular area described of radius c, perpendicular to R. Let r be the distance of the centre of B from the plane of that area. Then

$$\frac{dr}{dt} = R.$$

Let a be the distance from O, the centre of A, to the point P, in which the line through the centre of B parallel to R cuts that plane. Then, if $a < c$, a collision will occur between A and B, unless any third sphere previously collides with either of them. Further, a^2+r^2 cannot be less than c^2. And, if a^2+r^2 is infinitely nearly equal to c^2, the chance of any third sphere colliding with either A or B before they collide with each other vanishes, and a collision necessarily occurs between A and B. The only effect of that collision is to change the direction of the relative velocity R; and the nature of that change depends only on a, and on the angle β, which OP makes with a fixed diameter of the circular area.

Let us call a, β the *collision coordinates*. If the velocities of the two colliding spheres before collision be denoted by

$$\left.\begin{matrix} u \;\ldots\; u+du \\ v \;\ldots\; v+dv \\ w \;\ldots\; w+dw \end{matrix}\right\} \text{ for one sphere,}$$

and

$$\left.\begin{matrix} U \;\ldots\; U+dU \\ V \;\ldots\; V+dV \\ W \;\ldots\; W+dW \end{matrix}\right\} \text{ for the other,}$$

and if the collision coordinates be $\alpha \dots \alpha + d\alpha$, and $\beta \dots \beta + d\beta$, then as the result of collision u, v, w, U, V, W become u', v', w', U', V', W', and α, β become α', β'. Conversely, if before collision the variables be denoted by the accented letters, their values after collision will be denoted by the unaccented letters, and, as is known,

$$du\, dv\, dw\, dU\, dV\, dW = du'\, dv'\, dw'\, dU'\, dV'\, dW'.$$

6. Let the number per unit volume of spheres whose velocities are $u \dots u+du$, $v \dots v+dv$, $w \dots w+dw$ be $f(u, v, w)\, du\, dv\, dw$. Call these the class u. Similarly, let the number whose velocities are $U \dots U+dU$, &c., be $F(U, V, W)\, dU\, dV\, dW$, and call these the class U. Now, let us suppose for a moment that no collisions are allowed to happen, except (1) direct collisions between the spheres of class u and spheres of class U, without restriction as to the values of α and β; and (2) reverse collisions between spheres of class u' and spheres of class U', with such values only of α' and β' as that u', v', w', &c., shall after collision become $u \dots u+du$, &c.

If that were so, the only way by which any sphere could leave the class u would be by one of the direct collisions, and the only way by which any sphere could enter the class u would be by one of the reverse collisions. Hence on this supposition the increase per unit of time of the number of spheres in the class u, *i.e.*,

$$\frac{d}{dt} f(u, v, w), \quad \text{or} \quad \frac{df}{dt},$$

would be (number of reverse collisions per unit of time) — (number of direct collisions per unit of time).

7. Now, in the ordinary case, when f, F are independent, the number of direct collisions is

$$\iint \pi c^2 R f F \,.\, d\alpha\, d\beta.$$

And the number of reverse collisions is

$$\iint \pi c^2 R f' F' \,.\, d\alpha\, d\beta,$$

and so
$$\frac{df}{dt} = \iint \pi c^2 R\, (f'F' - fF)\, d\alpha\, d\beta.$$

8. But I now propose to treat the case in which f and F are not

independent, or the velocities u, U are *correlated.* And, therefore, for fF we must substitute a more general form

$$\phi\,(u,\,v,\,w,\,U,\,V,\,W,\,\alpha,\,\beta),$$

where ϕ is some function.

For the reverse collisions we shall have a corresponding function

$$\phi'\,(u',\,v',\,w',\,U',\,V',\,W',\,\alpha,\,\beta) \quad \text{or} \quad \phi'.$$

Then, collisions being still restricted as stated in 6, we should have

$$\frac{df}{dt} = \iint \pi c^2 R\,(\phi'-\phi)\,d\alpha\,d\beta.$$

9. But now we can make U, V, W assume successively all values, still maintaining u, v, w unaltered; and then we obtain for the complete variation of f with the time

$$\frac{df}{dt} = \iiiint\!\!\int \pi c^2 R\,(\phi'-\phi)\,d\alpha\,d\beta\,dU\,dV\,dW.$$

Now, let
$$H = \iiint f\,(\log f-1)\,du\,dv\,dw\,;$$

and therefore

$$\frac{dH}{dt} = \iiint \frac{df}{dt}\log f\,du\,dv\,dw$$
$$= \iiint du\,dv\,dw \iiiint\!\!\int \pi c^2 R\,(\phi'-\phi)\,\log f\,d\alpha\,d\beta\,dU\,dV\,dW.$$

10. In this integration, extending over all values both of u, v, w and U, V, W, these classes interchange, so that our integral includes the two terms

$$\pi c^2 R\,(\phi'-\phi)\,\log f$$

and

$$\pi c^2 R\,(\phi'-\phi)\,\log F;$$

and therefore includes the term

$$\pi c^2 R\,(\phi'-\phi)\,\log\,(fF).$$

For a similar reason it includes the term

$$\pi c^2 R\,(\phi-\phi')\,\log\,(f\,F')\,;$$

and therefore includes the term

$$\pi c^2 R\,(\phi'-\phi)\log\frac{fF}{f'F'},$$

and consists wholly of terms of this form.

11. Thus expressed, $\frac{dH}{dt}$ is not necessarily always of the same sign, unless of the two equations

$$\phi = \phi', \quad fF = f'F'$$

one involves the other (which condition, however, will be found to hold in the cases we shall consider). But in the permanent state $\frac{dH}{dt}$ must be zero, which can be by making either

$$\phi = \phi' \quad \text{or} \quad fF = f'F'.$$

Also $\frac{df}{dt}$ must be zero, which can only be by making

$$\phi = \phi'.$$

If, therefore, in any problem we find that the two equations

$$\phi = \phi' \quad \text{and} \quad fF = f'F'$$

cannot co-exist, but one must be taken and the other left, we must take

$$\phi = \phi'.$$

In our case, however, we shall find that the solution of

$$\phi = \phi'$$

involves $$fF = f'F'.$$

12. A solution of this equation

$$\phi = \phi'$$

is obtained by making ϕ a function of the energy only, namely, the ordinary solution

$$\phi = K\epsilon^{-h(u^2+v^2+w^2+U^2+V^2+W^2)}.$$

But, as Mr. Bryan has pointed out, in his "Report on Thermodynamics," that is not the only solution. And it must be rejected here because it makes the velocities of colliding spheres independent, which is assumed not to be true.

13. The following is another solution, namely,

$$\phi = K\epsilon^{-hQ},$$

in which $Q = A\,(u^2+v^2+w^2+U^2+V^2+W^2)+B\,(uU+vV+wW)$

and K, A, B are constant.

For, using this form, we have, after collision,

$$Q' = A\,(u'^2+v'^2+w'^2+U'^2+V'^2+W'^2)+B\,(u'U'+v'V'+w'W').$$

Now, by the conservation of energy,

$$u'^2+v'^2+w'^2+U'^2+V'^2+W'^2 = u^2+v^2+w^2+U^2+V^2+W^2,$$

and, by conservation of R or R^2,

$$(u'-U')^2+(v'-V')^2+(w'-W')^2 = (u-U)^2+(v-V)^2+(w-W)^2;$$

and therefore also

$$u'U'+v'V'+w'W' = uU+vV+wW;$$

and therefore $\qquad Q' = Q$

and $\qquad \phi' = \phi.$

14. Assuming that our function ϕ contains the velocities of two spheres only, we find $f(u, v, w)$ or f by integrating ϕ according to U, V, W between limits $\pm\infty$, and find F, f', and F' in the same way. Whence it is easily seen that

$$\phi = \phi'$$

involves $\qquad fF = f'F',$

and so the function H found on our hypothesis has all the properties of that function as usually found on the hypothesis that $B = 0$. But *the actual value attained by H when minimum* will be a function of B.

15. Now let us consider a more general case, that the velocities, not of two only, but of n, spheres are correlated.

Let us suppose that a certain spherical space S contains n spheres, and that, their positions being unknown, the chance of their having velocities

$$u_1 \ldots u_1+du_1 \ldots w_n \ldots w_n+dw_n$$

is of the form $K\epsilon^{-hQ}$, in which

$$Q = (au_1^2 + bu_1u_2 + au_2^2 + bu_1u_3 + bu_2u_3 + \&c.),$$

and K, a, b are constants.

In order that our system may be permanent, that is, unaffected by collisions, it is necessary and sufficient that when, by collision of any pair of spheres, their velocities u_1, v_1, w_1, u_2, v_2, w_2, become u_1', v_1', &c., all the terms in the index should remain with u_1', v_1', &c., substituted for u_1, v_1, &c., that is, if Q contain au_1^2, Q' must contain $au_1'^2$, and so on.

16. Let us then denote by λ, μ, ν the direction cosines of the line of centres at collision between the two spheres whose velocities are before collision $u_1\,v_1\,w_1$, $u_2\,v_2\,w_2$. Their velocities resolved in the line of centres are $\lambda u_1 + \mu v_1 + \nu w_1$ and $\lambda u_2 + \mu v_2 + \nu w_2$. And these are interchanged by the collision, so that after collision

$$u_1' = u_1 - \lambda\,(\lambda u_1 + \mu v_1 + \nu w_1) + \lambda\,(\lambda u_2 + \mu v_2 + \nu w_2),$$

and, to determine $u_1' \ldots w_2'$, we have the six linear equations

$$\begin{aligned}
u_1' &= (1-\lambda^2)\,u_1 - \lambda\mu v_1 - \lambda\nu w_1 + \lambda^2 u_2 + \lambda\mu v_2 + \lambda\nu w_2,\\
v_1' &= -\lambda\mu u_1 + (1-\mu^2)\,v_1 - \mu\nu w_1 + \lambda\mu u_2 + \mu^2 v_2 + \mu\nu w_2,\\
w_1' &= -\lambda\nu u_1 - \mu\nu v_1 + (1-\nu^2)\,w_1 + \lambda\nu u_2 + \mu\nu v_2 + \nu^2 w_2;\\
u_2' &= \lambda^2 u_1 + \lambda\mu v_1 + \lambda\nu w_1 + (1-\lambda^2)\,u_2 - \lambda\mu v_2 - \lambda\nu w_2,\\
v_2' &= \lambda\mu u_1 + \mu^2 v_1 + \mu\nu w_1 - \lambda\mu u_2 + (1-\mu^2)\,v_2 - \mu\nu w_2,\\
w_2' &= \lambda\nu u_1 + \mu\nu v_1 + \nu^2 w_1 - \lambda\nu u_2 - \mu\nu v_2 + (1-\nu^2)\,w_2.
\end{aligned}$$

To solve these equations for u_1, v_1, &c., we have only to interchange the accents between the right and left hand members.

17. If, now, in the expression

$$Q = au_1^2 + bu_1u_2 + au_2^2 + bu_1u_3 + bu_2u_3 + \&c.,$$

we substitute for u_1, u_2, and similarly for v_1, v_2, w_1, w_2, their values in terms of u_1', u_2', &c., we find

(1) The coefficient of $u_1'^2$ is a. That is because u_1^2 and u_2^2 have the same coefficient a in Q.

(2) The coefficient of $u_1'u_2'$ is b, the same as before for u_1u_2.

(3) The coefficient of $u_1'u_3$ is b, the same as for u_1u_3, &c.

The form of the index is therefore unaltered, and the assumed law of distribution is unaffected by collisions.

18. We can now find the chance that two of the n spheres shall have velocities $u_1 \dots u_1+du_1$, &c., and $u_2 \dots u_2+du_2$, &c., whatever the velocities of the others may be, by integrating ϕ according to $u_3, v_3 \dots w_n$ between the limits $\pm\infty$. As no products of the form uv, uw, or vw are supposed to occur in Q, it is sufficient to operate on the u's only.

Form then the determinant of the function Q, that is,

$$D = \begin{vmatrix} 2a, & b, & b, & \dots & b \\ b, & 2a, & b, & \dots & b \\ \dots & \dots & \dots & \dots \end{vmatrix},$$

in all n^2 constituents. Let D_{11}, D_{12}, &c., be its first minors, and D_{1221} the coaxial minor formed by omitting the first and second rows and columns. Then the result of the integration is

$$\epsilon^{-hA(u_1^2+\dots+u_2^2+\dots)+B(u_1u_2+\dots)},$$

in which $$A = \frac{D_{11}}{D_{1221}}, \quad B = \frac{D_{12}}{D_{1221}}.$$

But, evaluating the determinant, we find

$$D = (2a-b)^n + nb\,(2a-b)^{n-1}.$$

This is easily seen for $n = 2$, $n = 3$, and can be extended by induction.

Therefore also

$$D_{11} = (2a-b)^{n-1} + (n-1)\,b\,(2a-b)^{n-2},$$

$$D_{1221} = (2a-b)^{n-2} + (n-2)\,b\,(2a-b)^{n-3}.$$

Also we find $$D_{12} = b\,(2a-b)^{n-2}.$$

Therefore $$A = (2a-b)\,\frac{2a+\overline{n-2}\,b}{2a+\overline{n-3}\,b},$$

$$B = \frac{b\,(2a-b)}{2a+\overline{n-3}\,b}.$$

We can now treat the function H as in 13.

19. Again, if we integrate once more, we can find the chance that a single sphere shall have velocities $u \ldots u+du$, &c., in the form

$$K\epsilon^{-hD/D_{11}(u^2+v^2+w^2)}\,du\,dv\,dw = f(u, v, w)\,du\,dv\,dw,$$

whence also for two colliding spheres

$$fF = f'F'.$$

And from that result we find that H exceeds the value which it has when $b = 0$ by $\frac{1}{2}\log\frac{D}{D_{11}}$, and the function H has for this system all its ordinary properties, becoming minimum in the assumed distribution, and having when minimum the last stated value.

20. We must consider further the coefficients a and b.

The integration in 18 extended over n spheres supposed to be contained in a spherical space S, so that, ρ being the number of spheres in unit of volume, $n = \rho S$. As S becomes very large, the chances for the two spheres, whose positions within S are unknown, having given velocities must approach independence, that is, A becomes constant and B tends to zero. Comparing this with the values found above for A and B, we see that for large values of S (or of n) $2a-b$ is independent of S, and b tends to vanish. That is one condition which a and b have to satisfy. Another can be found as follows.

21. On the equilibrium of a vertical column of gas whose molecules are equal elastic spheres of diameter c.

If in the Clausian equation

$$\tfrac{3}{2}pV = \Sigma\tfrac{1}{2}mv^2 + \tfrac{1}{2}\Sigma\Sigma Rr,$$

we evaluate the virial term $\frac{1}{2}\Sigma\Sigma Rr$, we find it equal in case of our elastic spheres to $\frac{2}{3}\pi c^3\rho \,.\, 2\rho T_r$. Here T_r is the energy of the motion of the spheres in the volume considered relative to their common centre of gravity. (See *Science Progress*, November, 1894.)

$$\text{Let}\quad \tfrac{2}{3}\pi c^3\rho = \kappa = \frac{4\times\text{aggregate volume of spheres in volume } V}{V}$$

Then we know that p, or the pressure per unit of surface, is equal to $(1+\kappa)\,\frac{2}{3}\rho T_r$.

22. I find now that in a vertical column of gas whose molecules are equal elastic spheres of diameter c it is not T that is constant, as

proved by Maxwell for the case where c (and therefore κ) is negligible, but

$$\cdots\ T+\kappa T_r.$$

(See Appendix.)

$$\text{Also } T+\kappa T_r = a\,(u_1^2+u_2^2+\ldots+w_n^2)+b\,(u_1u_2+u_1u_3+\ldots+v_1v_2+\&\text{c.}),$$

if we make

$$2a = 1+\frac{n-1}{n}\kappa,$$

$$b = -\frac{\kappa}{n} = -\tfrac{2}{3}\,\frac{\pi c^3}{S},$$

because

$$n = \rho S.$$

The coefficients a and b so found satisfy the condition of 20 above. Also the distribution of velocities according to this law is unaffected by collisions, as shown in 17. Therefore it gives a more general solution of the problem of the motion of elastic spheres than the ordinary one in which the velocities of each sphere are supposed to be independent. Also, with these values of a and b,

$$D = (1+\kappa)^{n-1} \quad \text{and} \quad D_{11} = (1+\kappa)^{n-2}.$$

The value of H found for this system is

$$H = \tfrac{3}{2}\log h+\tfrac{3}{2}\log\frac{D}{D_{11}}+\text{constant}$$

$$= \tfrac{3}{2}\log h+\tfrac{3}{2}\log(1+\kappa)+\text{constant}.$$

The smaller n is, the greater in numerical value is the ratio $\frac{b}{a}$, and therefore the more intense the *correlation*.

23. The above values of a and b are to be regarded as limiting values which a and b assume when S, the space considered, is very large compared with $\frac{2}{3}\pi c^3$. For smaller values of S a correction is required, as follows.

Correction.

The limiting values assumed for a and b were

$$\left.\begin{aligned} 2a &= 1+\frac{n-1}{n}\kappa \\ b &= -\frac{\kappa}{n} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

The corrected values are

$$\left.\begin{aligned} 2a &= \frac{n+\kappa}{n}\left(1+\frac{n-1}{n}\kappa\right) \\ b &= -\frac{n+\kappa}{n}\frac{\kappa}{n} \end{aligned}\right\} \quad \text{.....................(2),}$$

which also satisfy the condition of 20.

I assume the chance for a (spherical) group of n contiguous spheres, whose positions within the sphere are unknown, having velocities infinitely near to $u_1, v_1, \ldots w_n$, &c., to be $C\epsilon^{-hQ}\,du_1 \ldots$ with

$$Q = a\Sigma\,(u^2+v^2+w^2) + b\Sigma\Sigma\,(uu'+vv'+ww').$$

Now, if this be true, the chance for any single sphere having velocity in x, $u_1 \ldots u_1+du_1$ is found by integrating $\epsilon^{-hQ}\,du_1 \ldots dw_n$ for all the variables except u_1 between $\pm\infty$, and comes out in the form

$$\epsilon^{-h(D/D_{11})u_1^2}\,du,$$

in which
$$D = \begin{vmatrix} 2a, & b, & b \ldots \\ b, & 2a, & b \ldots \\ \ldots & \ldots & \ldots \end{vmatrix},$$

and D_{11} is its first coaxial minor.

Now, to be consistent, this chance must be the same, whether we regard the single sphere as a member of a group of n, or as a member of a group of $2n$, &c., so long at least as ρ or $\frac{n}{S}$ is constant. Therefore $\frac{D}{D_{11}}$ must for all values of n be independent of n, except as it appears in $\frac{n}{S}$. But, with the values (1) of a and b,

$$\frac{D}{D_{11}} = (1+\kappa)\frac{n}{n+\kappa}.$$

Therefore, with the values (2) of a and b,

$$\frac{D}{D_{11}} = (1+\kappa) = 1+\frac{ns}{S},$$

if
$$s = \tfrac{2}{3}\pi c^3,$$

and that is the solution.

24. With these values (2) of a and b, the index becomes

$$h\frac{n+\kappa}{n}(T+\kappa T_r),$$

or

$$h\frac{S+s}{S}(T+\kappa T_r),$$

which becomes in limit, when $\frac{S}{s}$ is large, $T+\kappa T_r$ whatever the density, or $\frac{n}{S}$, may be. Without affecting the above results, we may by a further small correction of $2a$ and b cause the determinant to vanish when the density $\frac{n}{S}$ exceeds a certain point, beyond which point therefore the formulæ may cease to be applicable.

APPENDIX.

To prove the above stated result for the vertical column.

1. If p be the pressure per unit of surface, x the height of a point in the column above a fixed plane, f the vertical force, m the mass of a sphere, ρ the density, we have

$$\frac{dp}{dx} = -mf\rho,$$

also

$$p = \tfrac{2}{3}(1+\kappa)\rho T_r.$$

Here

$$\kappa = \tfrac{2}{3}\pi c^3\rho,$$

and T_r is kinetic energy of relative motion; whence, if we make

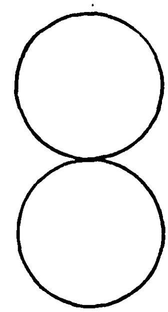
$$(1+\kappa)T_r = \text{constant} = \frac{3}{2h},$$

we find

$$\rho = \rho_0 e^{-hmfx},$$

which is the same equation as found for the ordinary case when $c = 0$ and $\kappa = 0$.

2. Again, consider N spheres crossing the plane $x = 0$ with u for vertical component of velocity. Of these some, say $N-N'$, will reach the plane $x = dx$ without collision. N' will undergo collision before reaching dx. But for these N' there will be substituted, as the result of collisions, N' other spheres with the same vertical component u.



Now, if the impact were direct, *i.e.*, the line of centres at collision vertical, the substituted sphere would gain a vertical height c, *i.e.*, the diameter of a sphere, without losing in respect of that distance any kinetic energy to the force f. This is a consequence of the fundamental assumption of instantaneous impacts, for which I am not responsible. The conservation of energy is not affected, because whatever kinetic energy one sphere gains the other loses. If, therefore, all the N' collisions were direct, the average height of the N spheres at the end of the time $\frac{dx}{u}$ would be, not dx, but $dx+\frac{N'}{N}c$, while their loss of kinetic energy would be $Nmfdx$.

3. But all impacts will not be direct; we must consider then the result of indirect impacts. For this purpose consider two classes of collisions, in one of which the sphere A has vertical component u before collision, and in the other A' has vertical component u after collision. The effect of a pair of collisions, one from each class, is to substitute A' for A as the sphere with vertical component u. Now let l denote the vector line of centres at collision, and $\cos(ul)$ the cosine of the angle which l makes with the vertical. Then in the first of the pair of collisions the centre of A is below the point of contact by $\frac{1}{2}c\cos(ul)$. In the second, the centre of A' is above the point of contact by $\frac{1}{2}c\cos(ul)$. There is no reason why the point of contact should be higher or lower in one case than in the other. It will be on average at the same height. Therefore on average of all pairs of collisions substituting A' for A with vertical velocity u, A' is above A by

$$\overline{c\cos(ul)} = r, \text{ suppose.}$$

Let q be the relative velocity of the two colliding spheres. Then

$$\begin{aligned} r &= \overline{c\cos(ul)} \\ &= \overline{c\cos(uq)}\;\overline{\cos(ql)} \\ &= \tfrac{2}{3}\overline{c\cos(uq)}, \end{aligned}$$

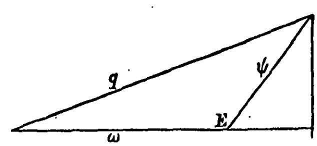
because $$\overline{\cos(ql)} = \frac{\int\cos^2\theta\sin\theta\,d\theta}{\int\cos\theta\sin\theta\,d\theta} = \tfrac{2}{3}.$$

Let ω be the absolute velocity of the sphere whose vertical component velocity is u, so that

$$\cos(u\omega) = \frac{u}{\omega},$$

Then
$$r = \tfrac{2}{3}c\,\overline{\cos(uq)}$$
$$= \tfrac{2}{3}c\,\frac{u}{\omega}\,\overline{\cos(\omega q)}.$$

Let ψ be the velocity of the other colliding sphere, E the angle between ω and ψ. Then



$$r = \tfrac{2}{3}c\,\frac{u}{\omega}\,\frac{\omega - \psi\cos E}{q}.$$

We have to multiply this by the number of collisions which N spheres having velocity ω undergo with spheres of velocity $\psi \ldots \psi + d\psi$, making with ω angles $E \ldots E + dE$ in time dt, or $\frac{dx}{u}$, and then integrate for all values of ψ and E.

Let $\rho f(\psi)\,d\psi$ be the number of spheres in unit volume with velocity $\psi \ldots \psi + d\psi$. The result is

$$N\pi c^2\rho \int_0^\infty d\psi\, f(\psi) \int_0^\pi \tfrac{1}{2}\sin E\, dE\, q\, \tfrac{2}{3}c\,\frac{u}{\omega}\,\frac{\omega - \psi\cos E}{q}\,\frac{dx}{u}$$
$$= \tfrac{2}{3}\pi c^3\rho\,.\,Ndx$$
$$= \kappa N dx.$$

Therefore at time dt the average height of the N spheres or their successors above the plane $x = 0$ is $(1+\kappa)\,dx$.

But the energy which they lose in the ascent is $Nmfdx$. The loss takes place only during free path. It follows that the loss of energy due to the ascent dx is, allowing for substitutions, $\frac{mfdx}{1+\kappa}$ per sphere.

4. Now suppose that at $x = 0$ the number per unit of volume of spheres having $\frac{1}{2}mu^2 \ldots d(u^2)$ for energy of vertical velocity to be

$$K e^{-h(1+\kappa)mu^2}\, d(u^2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

Then, by what has been proved in (2), the number which at height dx have $\frac{1}{2}mu^2 \ldots d(u^2)$ for energy of vertical velocity is

$$e^{-hmfdx}\, K e^{-h(1+\kappa)mu^2}\, d(u^2),$$

and the number which at height dx have

$$\tfrac{1}{2}mu^2 \dots d\,(u^2) - \frac{mfdx}{1+\kappa}$$

for energy of vertical velocity is

$$\epsilon^{-hmfdx}\, K\epsilon^{-h(1+\kappa)[mu^2-(mfdx)/(1+\kappa)]}\, d\,(u^2) = K\epsilon^{-h\overline{1+\kappa}\,mu^2}\, d\,(u^2) \dots\dots (2).$$

The two groups (1) and (2) are equally numerous, and therefore either can by ascending or descending, allowing for substitutions, exactly replace the other. Now this is the reasoning by which in the ordinary case, when $\kappa = 0$, we prove T to be constant. It now proves $(1+\kappa)\,T_r$ to be constant.

5. Further, any group of n spheres will generally have some energy of motion of their common centre of gravity, or, as Natanson calls it, apparent motion, of which we have as yet taken no account. Call this T_s. Then T_s is independent of x for the same reason that when $c = 0$ T is independent of x. Therefore $T_s + \overline{1+\kappa}\,T_r$ or $T + \kappa T_r$ is independent of x.

6. The pressure per unit of surface is increased in the ratio $1 : 1+\kappa$ as the molecules, from being material points, become spheres with finite diameter c.

But the pressure per unit of surface is the quantity of momentum which is carried through unit of surface in unit of time (Watson, *Kinetic Theory of Gases*). Now, so far as this momentum is carried through the surface by molecules *during their free path*, it is not altered in the least by κ acquiring finite value. The increase of the transfer of momentum consists wholly in the process above explained, namely, the instantaneous transfer of momentum through the distance c which occurs on collision.