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On the Application of the Kinetic Theory to Dense Gases

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I. *On the Application of the Kinetic Theory to Dense Gases.*

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The motion of a great number of elastic spheres, when their aggregate volume does *not* bear an evanescent ratio to the containing space, has received little attention from writers on the kinetic theory. In what respect, beyond the shortening of the mean free path, will it differ from that of the rare medium usually discussed? I think that the answer to this question is that there exists in all systems, dense or rare, a tendency for the spheres to move together in masses or streams, and so to diminish the mean pressure per unit of area, and the number of collisions per unit of volume and time. And this tendency has an appreciable influence on the form of the motion as soon as the ratio of the aggregate volume of the spheres to the containing space becomes appreciable.

If a part of the system, say n spheres, be at any instant contained in a volume V, they have energy, T_s, of the motion of their common centre of gravity. And they have energy, T_r, of relative motion. As the spheres increase in diameter, the ratio T_r/T_s will be found to diminish on average. But the number of collisions per unit of volume and time, given T, or $T_r + T_s$, depends on T_r, and therefore diminishes by the diminution of T_r.

1. Let M be the mass, c the diameter of a sphere, ρ the number of spheres per unit of volume, p the pressure per unit of surface. Also let us now denote by ρT_r the energy of the motion of the ρ spheres relative to their common centre of gravity, so that T_r is now the mean value per sphere of this energy.

We have then, as is well known,

$$p = \tfrac{2}{3}\rho T_r + \tfrac{1}{3}\Sigma\Sigma Rr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

in which R is the repulsive force, r the distance between a pair of spheres, and the summation includes all pairs in unit of volume. We must first evaluate $\Sigma\Sigma Rr$ on the assumption that no forces act except during collisions.

2. Let q be the relative velocity of two spheres. Let θ be the angle made with q by the line of centres at collision, if a collision takes place. The angle θ may have any value from zero to $\frac{1}{2}\pi$. As the effect of collision the velocity, $\frac{1}{2}q\cos\theta$, in the line of centres is reversed for each sphere. We may assume this reversal to be effected

by the constant finite force $Mq \cos \theta/2dt$ acting on each sphere in the line of centres during the small time $2dt$.

Let us define this short but finite time $2dt$ as the time during which the two spheres *are in collision*, or the *duration of a collision*. Then, during collision, if dt be small enough, the virial of the supposed force is sensibly constant, and we calculate its value as follows. Let λ, μ, ν, be the direction cosines of the line of centres referred to any axes. The coordinates of the point of contact shall be x, y, z. Then those of the centres of the two spheres are, c being the diameter of either sphere,

$$x + \tfrac{1}{2}\lambda c, \quad y + \tfrac{1}{2}\mu c, \quad z + \tfrac{1}{2}\nu c \text{ for one sphere,}$$
$$\text{and } x - \tfrac{1}{2}\lambda c, \quad y - \tfrac{1}{2}\mu c, \quad z - \tfrac{1}{2}\nu c \text{ for the other.}$$

The component forces acting at the centre of the first sphere are

$$\lambda Mq \cos \theta/2dt, \qquad \mu Mq \cos \theta/2dt, \qquad \nu Mq \cos \theta/2dt.$$

Those acting at the centre of the second sphere are the same with reversed signs.

For two spheres colliding with relative velocity q we find that the virial is $cMq \cos \theta/2dt$ at each instant during collision. We have to multiply this by the chance that, given two spheres A and B with relative velocity q, they shall be in collision at any given instant.

It is assumed that we are dealing with a space throughout which T_r is constant, and therefore the fact that the relative velocity is q, affords no presumption with regard to the relative position of the two spheres. About the centre of sphere A suppose a spherical surface described with radius c. An element of that surface is $2\pi c^2 \cos \theta \sin \theta \, d\theta$. Upon that element of surface form the element of volume $2\pi c^2 \cos \theta \sin \theta \, d\theta \, qdt$. And form a similar element of volume on the other side of the sphere A, that is, using $\pi - \theta$ for θ. Then the two spheres are at this instant in collision if the centre of the sphere B is within either of those elements.

Let V be the volume in which n spheres are moving with T_r constant. Then by our assumption B is as likely to be in any part of V as in any other. Therefore the chance that A and B, having relative velocity q, are in collision, is

$$\frac{4\pi c^2 \cos \theta \sin \theta \, d\theta \, qdt}{V}.$$

The average virial for two spheres with relative velocity q is then at each instant

$$\int_0^{\pi/2} \frac{4\pi c^2 \cos \theta \sin \theta \, qdt}{V} \cdot c \cdot \frac{Mq \cos \theta}{2dt} \, d\theta$$
$$= M \frac{2}{3V} \pi c^3 q^2 = M \frac{2}{3V} \pi c^3 \{(u - u')^2 + (v - v')^2 + (w - w')^2\},$$

if u, v, w, u', v', w', be the component velocities of the two spheres. Now since $n\mathrm{T}_r$ is the energy of relative motion of n spheres in volume V,

$$n\mathrm{T}_r = \mathrm{M}\Sigma \frac{(u-u')^2 + (v-v')^2 + (w-w')^2}{2n},$$

the summation including every pair, and therefore

$$\Sigma\Sigma\mathrm{R}r = \tfrac{2}{3}\pi c^3 \frac{n}{\mathrm{V}} 2n\mathrm{T}_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$= \tfrac{2}{3}\pi c^3 \rho \,.\, 2n\mathrm{T}_r, \text{ since } \frac{n}{\mathrm{V}} = \rho.$$

Let $\frac{2}{3}\pi c^3 \rho = \kappa$. Then

$$\Sigma\Sigma\mathrm{R}r = \kappa \,.\, 2n\mathrm{T}_r \text{ for } n \text{ spheres in V},$$

$$\Sigma\Sigma\mathrm{R}r = \kappa \,.\, 2\rho\mathrm{T}_r \text{ for } \rho \text{ spheres in unit of volume.}$$

Substituting this value of $\Sigma\Sigma\mathrm{R}r$ in (1) we obtain

$$p = \tfrac{2}{3}(1+\kappa)\rho\mathrm{T}_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

It is assumed in these results that we are dealing with a space throughout which T_r is sensibly constant.

3. We see then that p is proportional to $\mathrm{T}_r + \kappa\mathrm{T}_r$. The analogy between this expression and BOLTZMANN'S $\mathrm{T} + \chi$, in which χ denotes potential energy, suggests that the law of distribution of velocities among our spheres should be, instead of $\epsilon^{-h\mathrm{T}}$ as in the rare medium, $\epsilon^{-h(\mathrm{T}_r + \kappa\mathrm{T}_r)}$, or rather, since there may be stream motion as well as relative motion, $\epsilon^{-h(\mathrm{T} + \kappa\mathrm{T}_r)}$.

Let us further develop this analogy. In the Clausian equation

$$\tfrac{3}{2}p\mathrm{V} = n\mathrm{T}_r + \tfrac{1}{2}\Sigma\Sigma\mathrm{R}r,$$

$$\tfrac{1}{2}\Sigma\Sigma\mathrm{R}r = \tfrac{2}{3}\pi c^3 \frac{n^2}{\mathrm{V}^2}\mathrm{T}_r,$$

where $n\mathrm{T}_r$ is the kinetic energy of the motion of n spheres in volume V relative to their common centre of inertia. Hence

$$p = \tfrac{2}{3}\left\{\frac{n}{\mathrm{V}} + \tfrac{2}{3}\pi c^3 \frac{n^2}{\mathrm{V}^2}\right\}\mathrm{T}_r.$$

If the n spheres, being initially contained in volume V_0, be compressed into volume V, and T_r be maintained constant during the process, the work done in compression is

$$\mathrm{W} = \int_{\mathrm{V}}^{\mathrm{V}_0} p\, d\mathrm{V} = \left\{\tfrac{2}{3}n\log\frac{\mathrm{V}_0}{\mathrm{V}} + \tfrac{4}{9}\pi c^3 n^2\left(\frac{1}{\mathrm{V}} - \frac{1}{\mathrm{V}_0}\right)\right\}\mathrm{T}_r.$$

The first term on the right-hand side expresses the work which would be done during the process if the spheres were material points, and no collisions took place between them. The second term expresses the amount by which this work is increased by the spheres having finite diameter c and undergoing collisions. And if V_0 be infinite, this additional work is

$$\tfrac{4}{9}\,\pi c^3\,\frac{n^2}{V}\,T_r, \quad \text{or} \quad \tfrac{2}{3}\,\kappa n T_r.$$

We see then that the term $n\kappa T_r$ in the index of $\epsilon^{-hn(T+\kappa T_r)}$ represents work done against collisions in compressing the system from an infinite volume to its actual volume with constant T_r. It is analogous to the potential χ in the usual expression $\epsilon^{-h(T+\chi)}$. It might not be inappropriate to call κT_r the *potential of collisions.*

In order to confirm or otherwise the above suggestion, I proceed to consider—

4. *The distribution of energy in a vertical column of gas when in equilibrium in a field of uniform force,* the molecules being equal elastic spheres of diameter c.

Let the column be an infinite cylinder, f, the force, being parallel to its axis.

Take a plane perpendicular to the axis as base, and let s be the height of a point above that plane. Then we have, with the same notation as before,

$$dp/ds = -Mf\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

and, as before,

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

Here T_r is the average per sphere of the energy of relative motion, which alone is concerned in p. But, in our vertical column, assume for the moment that there is no stream motion that need be taken into account, and, therefore, we may write T instead of T_r, and (3) becomes

$$p = \tfrac{2}{3}(1+\kappa)\,\rho T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3\text{A}).$$

Now κ contains ρ as a factor by (2). But I will now assume that, not $\overline{T}$, but $\overline{(1+\kappa)\,T}$, is independent of s, so that we may write $\overline{(1+\kappa)\,T} = 3/2h$ with h constant. On that assumption (3) and (4) give

$$\rho = \rho_0 \epsilon^{-hMfs} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

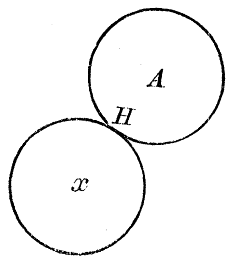
where ρ_0 is the value of ρ when $s = 0$.*

5. Now consider N spheres crossing the plane $s = 0$ with u for vertical component of velocity. Of these, say $N - N'$ reach the plane $s = ds$ without undergoing collision, N' will undergo collision before reaching ds. But for every collision by which one of the N is struck out, there will be another collision by which another sphere is

* See WATSON'S 'Kinetic Theory of Gases,' 2nd edition, pp. 56–66.

substituted for it, the substituted sphere having the same vertical velocity, *but not quite the same position on average*, as the original one had at the instant of its collision.

6. If the collision be direct, *i.e.*, the line of centres coincide with the relative velocity, the substituted sphere is advanced in position through a distance equal to c, in the direction of the line of centres, and that without any loss of kinetic energy by the action of the force f. If the collision be not direct, there is an advance, and we proceed to calculate its value. Let A be the centre of a sphere which comes out of collision with u for vertical component of velocity, x the centre of the sphere in collision with it, H the point of contact. Let l denote the vector line of centres xA,



and $\cos(ul)$ the cosine of the angle between l and s. Then $\frac{1}{2} c \cos(ul)$ is the projection of HA on the vertical, and $\overline{\frac{1}{2} c \cos(ul)}$ is its average value for all the collisions in question.

7. Again, let A′ be the centre of a sphere which enters collision with vertical velocity u, x' that of the sphere colliding with it, H the point of contact, and let l' denote the vector A′x'. Then, evidently $\overline{\frac{1}{2} c \cos(ul')} = \overline{\frac{1}{2} c \cos(ul)}$.

There will be as many collisions per unit of volume and time of the one class as of the other, and the height of the point of contact H, above the base, is on average the same for one class as for the other. Therefore, taking the collisions in pairs, one from each class, each pair substitutes A for A′ as the sphere with vertical velocity u; and, on average, the substituted sphere A is at the instant of its collision above the original sphere A′ at the instant of its collision by the distance $\overline{c \cos(ul)}$. We have next to show that on average of all collisions of N spheres taking place between $s = 0$ and $s = ds$, $c \cos(ul) = \kappa\, ds$, where $\kappa = \frac{2}{3} \pi c^3 \rho$.

8. Let ω be the actual velocity of the sphere A as it issues from collision, so that u is the vertical component of ω, and $\cos(u\omega) = u/\omega$. Let ψ be the velocity of the other sphere as it issues from collision with A, and E the angle between ω and ψ. Also let q be their relative velocity, so that $\cos(\omega q) = \dfrac{\omega - \psi \cos \mathrm{E}}{q}$.

Whatever be the values of ω, ψ, and E,

$$\overline{\cos(ul)} = \overline{\cos(uq)}\ \overline{\cos(ql)}$$

and
$$\overline{\cos(ql)} = \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \cos\theta \, d\theta \div \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \, d\theta = \frac{2}{3},$$
therefore
$$\overline{c \cos(ul)} = \frac{2c}{3} \overline{\cos(uq)}.$$

Again whatever be the values of ω, ψ, E,

$$\overline{\cos(uq)} = \overline{\cos(u\omega)}\ \overline{\cos(\omega q)}$$
$$= \frac{u}{\omega} \overline{\cos(\omega q)},$$
therefore
$$\overline{c \cos(ul)} = \frac{2c}{3} \frac{u}{\omega} \overline{\cos(\omega q)} = \frac{2c}{3} \frac{u}{\omega} \frac{\overline{\omega - \psi \cos \mathrm{E}}}{q}.$$

We have to multiply this expression by the number of collisions which N spheres, each having absolute velocity ω, undergo in time dt with other spheres having absolute velocity $\psi \ldots \psi + d\psi$; the angle between ω and ψ being $\mathrm{E} \ldots \mathrm{E} + d\mathrm{E}$, and then integrate according to ψ and E. That number is

$$\mathrm{N}\rho\pi c^2 q \, dt \, f(\psi) \, d\psi \, \tfrac{1}{2} \sin \mathrm{E} \, d\mathrm{E},$$

if $\rho f(\psi) \, d\psi$ be the number per unit of volume of spheres whose velocity is $\psi \ldots \psi + d\psi$, so that $\int_0^\infty f(\psi) \, d\psi = 1$.

Therefore the complete average value of $c \cos(ul)$, that is the average vertical displacement of the substituted spheres, is

$$\tfrac{2}{3} \mathrm{N}\rho\pi c^3 \, dt \int_0^\infty d\psi f(\psi) \int_0^\pi \tfrac{1}{2} \sin \mathrm{E} \, d\mathrm{E} \, q \frac{u}{\omega} \cos(\omega q),$$
or, since $dt = ds/u$,
$$\tfrac{2}{3} \mathrm{N}\rho\pi c^3 \, ds \int_0^\infty d\psi f(\psi) \int_0^\pi \tfrac{1}{2} \sin \mathrm{E} \, d\mathrm{E} \frac{q \cos(\omega q)}{\omega}.$$

But
$$\int_0^\pi \tfrac{1}{2} \sin \mathrm{E} \, d\mathrm{E} \frac{q \cos(\omega q)}{\omega} = \int_0^\pi \tfrac{1}{2} \sin \mathrm{E} \, d\mathrm{E} \frac{\omega - \psi \cos \mathrm{E}}{\omega} = 1,$$
also
$$\int_0^\infty f(\psi) \, d\psi = 1,$$
so our result is
$$\mathrm{N} \, \tfrac{2}{3}\pi c^3 \rho \, ds = \kappa \mathrm{N} ds.$$

We know (WATSON's 'Kinetic Theory of Gases,' 2nd edition, p. 56) that the quantity of vertical momentum transferred across the plane $s = 0$ per unit of area and time is proportional to p, and, therefore, increases in the ratio $1 : 1 + \kappa$, when the spheres, from being material points, acquire diameter c. We now see that this is true for each separate class of the vertical momenta.

9. Corresponding to N spheres with vertical velocity u at the plane $s = 0$ at the beginning of dt, we have at the end of dt N spheres, the same or substituted, whose average height is $(1 + \kappa)\, ds$ or $(1 + \kappa)\, u\, dt$. But their loss of kinetic energy due to the ascent is on average $\mathrm{M}f ds$ for each sphere. It follows that the average loss due to an ascent ds is, allowing for substitutions, $\frac{\mathrm{M}f ds}{1 + \kappa}$.

10. Let then the number per unit of volume of spheres whose energy of vertical velocity is $\frac{1}{2} u^2 \ldots \frac{1}{2} (u^2 + du^2)$ be at the base, where $s = 0$, $\rho_0 \epsilon^{-h\mathrm{Q}}\, du^2$ in which $\mathrm{Q} = \mathrm{M}\,(1 + \kappa)\,\frac{1}{2} u^2$ (A). Then the number per unit of volume which at height s have

$$\mathrm{M}\left(\frac{u^2}{2} - \frac{fs}{1 + \kappa}\right)$$

for energy of their vertical velocity is (remembering (5))

$$\rho_0 \epsilon^{-h\mathrm{M}fs}\, du^2 \epsilon^{-h(\mathrm{Q} - \mathrm{M}fs)},$$

that is $\rho_0 \epsilon^{-h\mathrm{Q}}\, du^2$ (B). The two classes A and B are equally numerous per unit of volume, and since, allowing for collisions and substitutions, the loss or gain of energy due to the force f in passing from the base to ds or *vice versâ* is $\mathrm{M}f ds/\overline{1 + \kappa}$, either class can by ascending or descending (the proper number of substitutions taking place) replace the other. And the assumed law of distribution of velocities is not disturbed by the force f, as spheres pass up and down the column. Now, make $\kappa = 0$ in the above reasoning, and we find it is exactly the reasoning from which, in the ordinary case of a rare medium, we conclude that T is constant throughout the column. The same reasoning leads in the general case to the conclusion that $(1 + \kappa)$ T is constant throughout.

11. The above results are obtained on the hypothesis that no account need be taken of stream motion among our spheres. If, however, there be such stream motion, we have to suppose that the N spheres crossing the plane $s = 0$ were members of a large group having a vertical velocity U of their common centre of gravity, and that the N spheres have vertical velocity u relative to this common centre of gravity. Then in time dt the N spheres will have risen on average the distance ds by virtue of their relative velocity u, where $u = ds/dt$, and a distance U dt by virtue of the common velocity U. Their loss of kinetic energy by the action of the force f in this ascent is

$$\mathrm{M}f\mathrm{U}\, dt + \mathrm{M}f\, ds/\overline{1 + \kappa},$$

or if U $dt = ds'$

$$\mathrm{M}f\,(ds' + ds/\overline{1 + \kappa}).$$

And now writing T_r for T, and T_s for the energy of the stream motion whose vertical component is U, we find that $T + \kappa T_r$ is constant throughout the column, and we may now write $T + \kappa T_r = 3/2h$.

12. It follows that we cannot express the law of distribution of velocities among the spheres in the form $C\epsilon^{-hT}$, or $C\epsilon^{-h\Sigma\frac{u^2+v^2+w^2}{2}}$, as in the rare medium, with $T = 3/2h$. The law must be $C\epsilon^{-hQ}$, in which Q is some quadratic function of the velocities. Suppose that for n spheres it is

$$Q_n = a_1 u_1^2 + b_{12} u_1 u_2 + a_2 u_2^2 + \&c.,$$

with corresponding expressions for the components v and w.

If we find the mean value of Q_n by integrating ϵ^{-hQ_n} for all values of u_1, u_2, &c., between the limits $\pm \infty$, we find, there being $3n$ variables or 3 component velocities for each sphere,

$$\overline{Q_n} = 3n/2h.$$

But

$$3n/2h = n\,(\overline{T + \kappa T_r}),$$

therefore,

$$\overline{Q_n} = n\,(\overline{T + \kappa T_r}).$$

This result might be considered to justify the assumption that the law of distribution of velocities is in all cases, including the field of no forces formed by making $f = 0$, accurately expressed as follows. The chance that the velocities of n spheres, forming a group together, shall be $u_1 \ldots u_1 + du_1$, &c., is proportional to $\epsilon^{-hn(T+\kappa T_r)}$, in which

$$nT = \tfrac{1}{2}M\Sigma\,(u^2 + v^2 + w^2)$$
$$nT_r = \tfrac{1}{2}M\Sigma\,\{(u-u')^2 + (v-v')^2 + (w-w')^2\}/n.$$

But we must remember that the whole treatment is based on the consideration of a great number of spheres, so that we cannot safely assume the law to hold when n is small. Let us, then, consider the subject from yet another point of view.

13. I have shown elsewhere ('Science Progress,' November, 1894), that in a dense medium the velocities of contiguous spheres cannot be independent of one another, because there is a presumption that recent collisions of two spheres near to one another have been with the same third sphere, and they have, so to speak, inherited some common velocity from it. In other words contiguous spheres have been exposed to the same environment, and, in the dense medium, environment does not change rapidly; therefore their velocities are not independent.

If, therefore, the spneres contained in a volume V be n in number, and their positions known, the chance that their velocities shall be

$$u_1 \ldots u_1 + du_1, \text{\&c.}, \qquad v_1 \ldots v_1 + dv_1, \text{\&c.},$$

must be of the form

$$C\epsilon^{-h(a_1u_1^2 + b_{12}u_1u_2 + a_2u_2^2 + \text{\&c.})},$$

in which the index is a quadratic function of u_1, u_2, &c., v_1, v_2, &c., and w_1, w_2, &c., but contains no products of the form uv, uw, or vw, and the coefficients b_{12}, &c., are functions of the positions of the spheres.

14. With regard to the forms of these coefficients, we observe that the quadratic function in the index must always be positive, because the chance cannot become infinite for infinite values of the variables, u. The condition for this is that the determinant

$$D = \begin{vmatrix} 2a_1, & b_{12}, & b_{13} \ldots & b_{1n} \\ b_{12}, & 2a_2, & b_{23}, \ldots & . \\ . & . & . & . \end{vmatrix},$$

and all its coaxial minors, must be positive, and, therefore, every a positive.

15. Again b_{12}, not being zero, expresses the fact that u_1 and u_2 are not independent. But it is also a fact that they are more likely to be of the same than of opposite signs. Therefore, b_{12}, and similarly every b, must be negative or zero.

16. Evidently also the coefficients b must generally diminish in absolute magnitude as the distance between the spheres to which they relate increases, and must become inappreciable at some distance, small compared with the dimensions of our system, but possibly large compared with the diameter of a sphere. The b's must be functions of the positions of the n spheres within V having this property.

Again we may consider either a volume V containing n spheres, or a smaller volume $\frac{n-1}{n}$ V containing $n - 1$ out of the n spheres, that is, all the n spheres except one, which one belongs to the outer layer. If the velocities of that one be denoted by u_n, v_n, w_n, and if Q_n be the quadratic function for the n spheres, Q_{n-1} for the $n - 1$ spheres, we must have

$$\epsilon^{-hQ_{n-1}} = \iiint_{-\infty}^{+\infty} \epsilon^{-hQ_n}\, du_n,\, dv_n,\, dw_n.$$

If we actually perform the integrations indicated for one variable, we get with

$$Q_n = a_1u_1^2 + b_{12}u_1u_2 + a_2u_2^2 + \text{\&c.}$$
$$Q_{n-1} = a'_1u_1^2 + b'_{12}u_1u_2 + a'_2u_2^2 + \text{\&c.},$$

in which

$$2a'_1 = 2a_1 - b_{1n}^2/2a_n, \qquad 2a'_2 = 2a_2 - b_{2n}^2/2a_n,$$
$$b'_{12} = b_{12} - b_{1n}b_{2n}/2a_n, \text{\&c.}$$

As the number of spheres included in our group diminishes, the coefficients a diminish, and, since every b is negative, the b's increase in absolute magnitude.

On the other hand, as n increases the a's increase, and every b^2, if changed at all, diminishes. Therefore, as u increases the function Q_n tends to a limiting form. But that limiting form must be nT if $\kappa = 0$, because in that case we know the law to be $\epsilon^{-h\mathrm{T}}$. We must then have ultimately $Q_n = n(\mathrm{T} + \kappa\theta)$, where θ is a quadratic function of the velocities. And we may now assume that *for a sufficiently great* number of spheres comprised in a group, throughout which κ is sensibly constant, the law is expressed by the function $C\epsilon^{-hn(\mathrm{T}+\kappa \mathrm{T}_r)}$, in which $C = \frac{1}{\sqrt{\pi}}\sqrt{D}$, D being the determinant of the coefficients of the quadratic function $\mathrm{T} + \kappa\mathrm{T}_r$.

We have thus obtained certain conditions which the coefficients a_1, b_{12}, &c., must satisfy. Another condition is that the assumed law of distribution of velocities expressed by the function

$$\epsilon^{-h(a_1 u_1^2 + b_{12} u_1 u_2 + \&c.)}$$

shall not be disturbed by a collision taking place between any two of the n spheres, which collision changes the velocities, but not the positions, of the two spheres in question. To find the values of a_1, b_{12}, &c., to satisfy this condition presents considerable difficulty. It is not, however, at present necessary to solve the problem in that form, as will be seen later. For we have only to consider the positions of the n spheres as unknown, and we obtain a solution sufficient for our purpose. If, namely, it be given that there are at any instant n spheres within a spherical space S, but nothing is known of their positions within S, we have only to assume that the chance of their having at that instant velocities $u_1 \ldots u_1 + du_1$, &c., is

$$\epsilon^{-hQ}\, du_1 \ldots dw_n,$$

with

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

containing only one coefficient a and one b, and we shall find that all necessary conditions are satisfied, including the condition that the assumed distribution shall be unaffected by collisions.

For let $x_1, y_1, z_1, x_2, y_2, z_2$ be the component velocities of two spheres before collision. A collision between the two converts these components into $x'_1, y'_1, z'_1, x'_2, y'_2, z'_2$ in the following manner. Let λ, μ, ν be the direction cosines of the line of centres at collision.

The velocities of the two spheres resolved in the line of centres are, before collision,

$$\lambda x_1 + \mu y_1 + \nu z_1 \quad \text{and} \quad \lambda x_2 + \mu y_2 + \nu z_2$$

respectively. And we have

$$x'_1 = x_1 - \lambda(\lambda x_1 + \mu y_1 + \nu z_1) + \lambda(\lambda x_2 + \mu y_2 + \nu z_2),$$
$$y'_1 = y_1 - \mu(\lambda x_1 + \mu y_1 + \nu z_1) + \mu(\lambda x_2 + \mu y_2 + \nu z_2),$$
&c.

That is,

$$x'_1 = (1-\lambda^2)x_1 - \lambda\mu y_1 - \lambda\nu z_1 + \lambda^2 x_2 + \lambda\mu y_2 + \lambda\nu z_2$$
$$y'_1 = -\lambda\mu x_1 + (1-\mu^2)y_1 - \mu\nu z_1 + \lambda\mu x_2 + \mu^2 y_2 + \mu\nu z_2$$
$$z'_1 = -\lambda\nu x_1 - \mu\nu y_1 + (1-\nu^2)z_1 + \lambda\nu x_2 + \mu\nu y_2 + \nu^2 z_2$$
$$x'_2 = \lambda^2 x_1 + \lambda\mu y_1 + \lambda\nu z_1 + (1-\lambda^2)x_2 - \lambda\mu y_2 - \lambda\nu z_2$$
$$y'_2 = \lambda\mu x_1 + \mu^2 y_1 + \mu\nu z_1 - \lambda\mu x_2 + (1-\mu^2)y_2 - \mu\nu z_2$$
$$z'_2 = \lambda\nu x_1 + \mu\nu y_1 + \nu^2 z_1 - \lambda\nu x_2 - \mu\nu y_2 + (1-\nu^2)z_2.$$

Call these equations A.

But inasmuch as the motion might take place the reverse way with the same values of λ, μ, ν, it must by the same reasoning be true that

$$x_1 = (1-\lambda^2)x'_1 - \lambda\mu y'_1 - \lambda\nu z'_1 + \lambda^2 x'_2 + \lambda\mu y'_2 + \lambda\nu z'_2, \text{ \&c.} \quad . \quad . \quad . \quad . \quad . \quad \text{A}',$$

which are the same as equations A with the accents interchanged between the right and left-hand members. If we solve either set of equations we get the other set.

17. Now it is given that at this instant the chance of the spheres having velocities $x_1 \ldots x_1 + dx_1$, &c., is $C\epsilon^{-hQ}\,dx_1 dx_2 \ldots$ in which

$$Q = ax_1^2 + bx_1x_2 + ax_2^2 + ay_1^2 + by_1y_2 + ay_2^2 + az_1^2 + bz_1z_2 + az_2^2$$
$$+ bx_1(x_3 + x_4 + \text{\&c.}) + \text{\&c.}$$
$$+ ax_3^2 + \text{\&c.} + \text{terms containing squares and products of the velocities } x_3 \ldots z_n.$$

The chance that after this collision the velocities of the n spheres shall have the values x'_1, y'_1, z'_1, x'_2, y'_2, z'_2, and x_3, y_3, &c., is found by substituting for x_1, y_1, z_1, x_2, y_2, z_2, in the index hQ, their values in terms of x'_1, y'_1, z'_1, x'_2, y'_2, z'_2, as given by equations A′. Effecting this substitution we find that the coefficient of x'^2_1 is

$$a\,.\{(1-\lambda^2)^2 + \lambda^2\mu^2 + \lambda^2\nu^2 + \lambda^4 + \lambda^2\mu^2 + \lambda^2\nu^2\}$$
$$+ b\,.\{\lambda^2(1-\lambda^2) - \lambda^2\mu^2 - \lambda^2\nu^2\}$$

that is a. Similarly, we find that the coefficient of $x'_1x'_2$ in the new index is b, and the coefficient of every product x'_1x_r in the new index is the same as that of x_1x_r in the original index. The new index is then the same function of x'_1, y'_1, z'_1, x'_2, y'_2, z'_2, that the original one was of x_1, y_1, z_1, x_2, y_2, z_2. The assumed distribution of velocities is therefore not affected by any one, and therefore not by any number of collisions.

This, it will be remembered, is on the assumption that all the coefficients a are the same, and all the coefficients b are the same, so far as they have to do with the colliding spheres.

18. Now

$$\frac{1}{M} n (T + \kappa T_r)$$
$$= \left(1 + \frac{n-1}{n}\kappa\right)\frac{u_1^2}{2} - \frac{\kappa}{n} u_1 u_2 - \frac{\kappa}{n} u_1 u_3 + \left(1 + \frac{n-1}{n}\kappa\right)\frac{u_2^2}{2} + \&c.$$
$$= a\Sigma (u^2 + v^2 + w^2) + b\Sigma\Sigma (uu' + vv' + ww'), \text{ if } 2a = 1 + \frac{n-1}{n}\kappa \text{ and } b = -\frac{\kappa}{n},$$

and if we use this for Q_n we find that all necessary conditions are satisfied, including the condition for permanence notwithstanding collisions.

19. If, however, the coefficients a, b were not the same for both colliding spheres, but the form were $a_1x_1^2 + b_{12}x_1x_2 + a_2x_2^2 + b_{13}x_1x_3 + b_{23}x_2x_3 + \&c.$, then we should find that the coefficient of x'^2_1 in the new index is $(1 - \lambda^2) a_1 + \lambda^2 a_2$; the coefficient of x'^2_2 is $(1 - \lambda^2) a_2 + \lambda^2 a_1$; the coefficient of $x'_1x'_2$ is as before, b_{12}; but that of x'_1x_3 is $(1 - \lambda^2) b_{13} + \lambda^2 b_{23}$; and that of x'_2x_3 is $(1 - \lambda^2) b_{23} + \lambda^2 b_{13}$.

The assumed law of distribution cannot in this case be unaffected by collisions, unless (1) all the a coefficients are the same; (2) if the velocities of the two colliding spheres be u_1, v_1, w_1 and u_2, v_2, w_2, and those of any third sphere be u_3, v_3, w_3, then $b_{13} = b_{23}$, that is, the b coefficients must be such functions of the position, that if spheres 1 and 2 are close together $b_{13} = b_{23}$, &c.

To return to the case of the positions of the spheres being unknown.

20. If we form the determinant of the system

$$D = \begin{vmatrix} \left(1 + \frac{n-1}{n}\kappa\right) & -\frac{\kappa}{n} & -\frac{\kappa}{n} & \cdot & \cdot & \cdot \\ -\frac{\kappa}{n} & \left(1 + \frac{n-1}{n}\kappa\right) & -\frac{\kappa}{n} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix},$$

we find

$$D = (1 + \kappa)^n - n\frac{\kappa}{n}(1 + \kappa)^{n-1}$$
$$D_{11} = (1 + \kappa)^{n-1} - \overline{n-1}\,\frac{\kappa}{n}(1 + \kappa)^{n-2}.$$

Hence we find

$$\overline{u_1^2} = \overline{u_2^2} = \&c. = \frac{D_{11}}{D} = \frac{1}{hM} \cdot \frac{1}{n} \cdot \frac{n + \kappa}{1 + \kappa},$$

therefore

$$n\text{T} = \frac{3}{2h} \cdot \frac{n+\kappa}{1+\kappa}.$$

Also

$$\overline{u_1 u_2} = \frac{\text{D}_{12}}{\text{D}}, \text{ \&c.}$$

[These results are easily obtained by considering the general determinant of n^2 constituents

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

in which all the axial constituents are $2a$, and all the non-axial constituents are b. It will be found for $n = 2$, $n = 3$, and thence by induction, that

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

Replacing $2a$ by $1 + \overline{n-1}\kappa/n$, and b by $-\kappa/n$, we get the result above stated.]

Also $\overline{v^2}$ and $\overline{w^2}$ have the same value as $\overline{u^2}$. And the whole kinetic energy of the n spheres, or $n\text{T}$, is, on average, $\text{M}\,\dfrac{3n\overline{u^2}}{2}$, or $n\text{T} = \dfrac{3}{2h}\,\dfrac{n+\kappa}{1+\kappa}$.

Again,

$$\frac{\kappa}{h\text{M}}\,n\text{T}_r = \kappa\,\frac{n-1}{2n}\,u_1^2 - \frac{\kappa}{n}\,u_1 u_2 - \frac{\kappa}{n}\,u_1 u_3 - \text{\&c},$$

$$+\,\kappa\,\frac{n-1}{2n}\,u_2^2 - \frac{\kappa}{n}\,u_2 u_3 - \text{\&c.},$$

$$- \text{\&c.},$$

with similar expressions for the v's and w's. But

$$\tfrac{1}{2}\left(1 + \kappa\,\frac{n-1}{n}\right)\overline{u^2} - \frac{\kappa}{n}\,\overline{u_1 u_2} - \text{\&c.} = \tfrac{1}{2}\left(1 + \kappa\,\frac{n-1}{n}\right)\frac{\text{D}_{11}}{\text{D}} - \frac{\kappa}{n}\,\frac{\text{D}_{12}}{\text{D}} - \text{\&c.} = 3n/2h\text{M}$$

by the properties of determinants.

Therefore

$$\kappa n\text{T}_r = \frac{3n}{2h} - \frac{3n}{2h}\,\frac{\text{D}_{11}}{\text{D}} = \frac{3n}{2h} - \frac{3}{2h}\,\frac{n+\kappa}{1+\kappa} = \frac{3}{2h}\,\frac{\overline{n-1}\,\kappa}{1+\kappa}$$

and

$$n\text{T}_r = \frac{3}{2h}\,\frac{n-1}{1+\kappa},$$

and therefore

$$n\text{T}_s = n\text{T} - n\text{T}_r = \frac{3}{2h}\left(\frac{n+\kappa}{1+\kappa} - \frac{n-1}{1+\kappa}\right) = 3n/2h,$$

and therefore $T_s/T = (1 + \kappa)/(n + \kappa)$, which increases as κ increases, that is, *cæteris paribus*, as the diameter c increases.

Again, the pressure per unit of area on a plane moving with the stream, and therefore the mean pressure, is $p = \frac{2}{3}(1 + \kappa)\rho T_r$, which is independent of the diameter c.

Now, the spheres being material points with $\overline{T_r} = 3/2h$, the mean pressure is $\frac{2}{3}\rho T_r$; that is, as we may write it, $\frac{2}{3}(1 + \kappa)\rho T_r$, because in this case $\kappa = 0$. As the spheres increase in diameter with $(1 + \kappa) T_r$ unaltered, the mean pressure per unit of area remains unaltered. In other words, it is exactly as much diminished by the conversion of part of the energy of relative motion of contiguous spheres into energy of stream motion as it is increased by the introduction of the term $\Sigma\Sigma Rr$ as the spheres acquire diameter c.

Comparing the actual value of p with what it would be if, with the same total kinetic energy, the spheres were material points, we see that it is diminished in the proportion $1 + \kappa : 1$.

The number of collisions per unit of volume and time is proportional to $c^2 T_r$; that is, to $\kappa^{\frac{2}{3}} / (1 + \kappa)$. It is less in the proportion $1 / (1 + \kappa)$ than it would be if, with the same total kinetic energy, the spheres had velocities independent of one another.

21. From the fact that p is independent of κ, it follows that local variations of density, *i.e.*, of κ, do not involve the expenditure of any work on the whole, and therefore such variations may and will come into being.

22. Boltzmann's minimum function continues to diminish by collisions, finally attaining its minimum constant value when the distribution of velocities defined by our assumption in 13 is established, but its actual value when minimum differs by $\frac{1}{2}\log D$ from what it would be if the spheres were material points.