

problem in itself has no physical meaning. For, according to the doctrine of the immobility of the æther, it is an absurdity to speak of forces acting upon or stresses existing in the æther.

Let us now consider this theory in its application to the electroidic phenomena of hydrodynamics. Just as well as an observer of these phenomena might arrive at Maxwell's views, he might, with his limited knowledge of the things before him, arrive at the views of Lorentz. But, as we see at once, they do not hold. For the hydrodynamic actions at a distance do depend upon a stress, although a much simpler one than that found by Maxwell.

The question to what extent it may be allowable to draw, from the electroidic phenomena of hydrodynamics, positive conclusions as to real electric phenomena may be open to discussion. The intimate nature of the analogy makes it very probable that useful suggestions may be obtained from this analogy. But of course the method must be tried with the greatest caution. The results produced here may perhaps encourage electricians to take up the stress-problem upon a wider base than Maxwell himself was able to do at his first attack upon this, *the* fundamental problem of the theory of electricity. The solution may be simpler than we expect. For the hydrodynamic results plainly show that even the simple isotropic stress may produce actions of the kind, which Maxwell supposed explicable only as the effect of a stress of the anisotropic type.

XLV. *On the Pressure of Gases and the Equation of Virial.*

By LORD RAYLEIGH, O.M., F.R.S.*

IF m be the mass of a particle, V its velocity, p the pressure and v the volume of the body composed of the particles, the virial equation is

$$\frac{1}{2} \sum m V^2 = \frac{3}{2} p v + \frac{1}{2} \sum \rho \phi(\rho), \quad . \quad . \quad . \quad (1)$$

where further ρ denotes the distance between two particles at the moment under consideration, and $\phi(\rho)$ the mutual force, assumed to depend upon ρ only. If the mutual forces can be neglected, either because they are non-existent or for some other reason, (1) coincides with Boyle's law, since the kinetic energy is supposed to represent temperature (T).

According to some experimenters, among whom may be especially mentioned Ramsay and Young, the relation between

* Communicated by the Author.

pressure and temperature at constant volume is in fact linear, or

$$p = T\psi(v) + \chi(v); \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and it is of interest to inquire whether such a form is to be expected on theoretical grounds, when $\phi(\rho)$ can no longer be neglected. It has indeed been maintained* that (2) is a rigorous consequence of the general laws of thermodynamics and of the hypothesis that the forces between molecules are functions of the distance only. The argument proceeded upon the assumption that the distances of the particles, and therefore the mutual forces between them, remain constant when the temperature changes, provided only that the volume of the body is maintained unaltered. According to this the virial term in (1) is a function of volume only, so that (1) reduces to (2), with $\psi(v)$ proportional to v^{-1} . But, as Boltzmann pointed out, the assumption is unfounded, and in fact inconsistent with the fundamental principles of the molecular theory. The molecules are not at rest but in motion; and when the temperature varies there is nothing to hinder the virial from varying with it.

The readiest proof of this assertion is by reference to the case where the molecules are treated as "hard elastic spheres," that is where the force is zero so long as ρ exceeds a certain value (the diameter of the spheres) and then becomes infinite. From the researches of Van der Waals, Lorentz, and Tait it is known that in that case

$$\frac{1}{2}\Sigma\rho\phi(\rho) = -\frac{1}{2}\Sigma mV^2 \cdot \frac{b}{v}, \quad . \quad . \quad . \quad . \quad (3)$$

where b , denoting four times the total volume of the spheres, is supposed to be small in relation to v . So far from the virial being necessarily independent of temperature, it is here directly proportional to temperature. The introduction of the special value (3) into (1) gives the well-known form

$$p(v-b) = \frac{1}{3}\Sigma mV^2 = RT, \quad . \quad . \quad . \quad . \quad (4)$$

in which b is still regarded as small in comparison with v . It is worthy of note that this particular case, although of course sufficient to upset the general argument that the virial is independent of temperature, nevertheless itself conforms to (2), proportionality to T being for this purpose as good as independence of T .

Not only is the linear relation maintained in spite of the forces of collision of elastic spheres when no other forces

* M. Levy, *C. R.* t. lxxxvii. pp. 449, 488, 554, 649, 676, 826 (1878).

operate, but it remains undisturbed even when we introduce such forces, provided that they be of the character considered in the theory of capillarity, that is extending to a range which is a large multiple of molecular distances and not increasing so fast with diminishing distance as to make the total effect sensibly dependent upon the positions occupied by neighbours. Under these restrictions symmetry ensures that the resultant force upon a sphere, situated in the interior and not undergoing collision, is zero; and the whole effect of such forces is represented (Young, Laplace, Van der Waals) by an addition to the pressure of a quantity independent of the temperature and inversely proportional to the square of the volume. In Van der Waals' well-known form

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the relation between p and T is still linear. Even if the particles depart from the spherical form, the virial of collisional and cohesive forces remains a linear function of the temperature*.

The forces above considered are partly repulsive and partly attractive. Repulsion at a certain degree of proximity seems to be demanded in order to preserve the individuality of molecules and to prevent infinite condensation. It will be remembered that Maxwell proposed a repulsion inversely as the *fifth* power of the distance, partly as the consequence of some faulty experiments upon the relation of viscosity to temperature and partly no doubt on account of a special facility of calculation upon the basis of this law. So far as viscosity (η) is concerned, its relation to temperature (T) when the force of repulsion varies as ρ^{-n} is readily obtained by the method of dimensions†. It appears that

$$\eta \propto T^{\frac{n+3}{2n-2}}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The case of sudden collisions may be represented by taking $n = \infty$, so that

$$\eta \propto T^{\frac{1}{2}}: \quad . \quad . \quad . \quad . \quad . \quad (7)$$

while if $n = 5$

$$\eta \propto T. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

According to experiments on the more permanent gases n

* "On the Virial of a System of Hard Colliding Bodies," 'Nature,' xlv. pp. 80-82 (1891); Scientific Papers, iii. p. 469.

† Proceedings Royal Society, lxi. p. 68 (1900); Scientific Papers, iv. p. 453.

would vary from .68 for hydrogen to 81 for argon ; but Sutherland's law*

$$\eta \propto \frac{T^{\frac{1}{2}}}{1 + C/T} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

probably represents the facts better than (6), whatever value may be assigned to n . According to the theory of corresponding states, C should be proportional to the critical temperature when we pass from one gas to another.

A similar application of the method of dimensions will give interesting information respecting the virial, when the force of repulsion is

$$\phi(\rho) = -\mu\rho^{-n}. \quad . \quad . \quad . \quad . \quad (10)$$

The virial is a definite function of N the number of molecules, m the mass of each molecule, V the velocity of mean square on which the temperature depends, μ the force at unit distance, and v the volume of the containing vessel. Of these quantities the virial is of the dimensions of energy, N has none, m is a mass simply, V is a velocity, v a volume, while μ has the dimensions

$$\text{mass} \times (\text{length})^{n+1} \times (\text{time})^{-2}.$$

Hence if we suppose that the virial varies as v^{-s} , we find that it must be proportional to

$$(mV^2)^{\frac{n-3s-1}{n-1}} \cdot \mu^{\frac{3s}{n-1}} \cdot v^{-s}; \quad . \quad . \quad . \quad (11)$$

or since mV^2 represents temperature,

$$T^{\frac{n-3s-1}{n-1}} \cdot \mu^{\frac{3s}{n-1}} \cdot v^{-s}. \quad . \quad . \quad . \quad (12)$$

For example, if $s=0$,

$$\Sigma\rho\phi(\rho) \propto T, \quad . \quad . \quad . \quad . \quad (13)$$

whatever n may be. Hence a term in the virial equation independent of volume must be proportional to temperature, as in (1). Again, if $s=1$,

$$\Sigma\rho\phi(\rho) \propto v^{-1} \cdot T^{\frac{n-4}{n-1}}. \quad . \quad . \quad . \quad (14)$$

Of this we have already had examples, both the virial terms in Van der Waals' equation being proportional to v^{-1} . The first, representing the virial of collisional forces, corresponds in (14) to $n=\infty$, giving proportionality to T . The second is independent of T and can be reconciled with (14) only by

* Phil. Mag. vol. xxxvi. p. 513 (1893).

supposing $n=4$. It might seem that in a rare gas, whenever the virial depends sensibly upon what occurs during the encounters of simple pairs of molecules, there must be proportionality to v^{-1} , so that (14) would apply. If, as Maxwell supposed, $n=5$,

$$\Sigma \rho \phi(\rho) \propto v^{-1} \cdot T^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (15)$$

in agreement with a result obtained by Boltzmann for this case. If we retain $n=5$, but leave the relation to v open, we get from (12)

$$\Sigma \rho \phi(\rho) \propto v^{-s} \cdot T^{1-\frac{3}{2}s}, \quad . \quad . \quad . \quad . \quad (16)$$

If we now discard the supposition that the dependence upon v follows the law of v^{-s} , we may interpret (16) to mean that considered as a function of v and T , the virial is limited to the form

$$\Sigma \rho \phi(\rho) = T \cdot F(vT^{\frac{3}{2}}), \quad . \quad . \quad . \quad . \quad (17)$$

F denoting an arbitrary function of the *single* variable $vT^{\frac{3}{2}}$.

And more generally, whatever n may be, we find from (12) that the virial is limited to the form

$$\Sigma \rho \phi(\rho) = T \cdot F\left(\frac{vT^{\frac{3}{n-1}}}{\mu^{\frac{3}{n-1}}}\right), \quad . \quad . \quad . \quad . \quad (18)$$

A further generalization may be made by discarding altogether the supposition that $\phi(\rho)$ is represented by any power of ρ . In this case it is convenient to write

$$\phi(\rho) = -\mu' f'(\rho/a), \quad . \quad . \quad . \quad . \quad (19)$$

where a is a linear quantity. Here f itself may be supposed to be of no dimensions, while μ' has the dimensions of a force. The virial is a function of μ' , a , m , V , v ; and since its dimensions are those of energy, *i. e.* of mV^2 or T , we may write

$$\Sigma \rho \phi(\rho) = T \cdot F(\mu', a, m, V, v),$$

where F is of no dimensions. It is easy to see that μ' , m , and V^2 can occur only in the combination μ'/mV^2 or μ'/T . To make this of no dimensions, we introduce the factor a . Thus F becomes a function of a , v , and $\mu'a/T$, in which again v can occur only in the form a^3/v . Accordingly

$$\Sigma \rho \phi(\rho) = T \cdot F\left(\frac{a^3}{v}, \frac{\mu'a}{T}\right), \quad . \quad . \quad . \quad . \quad (20)$$

F being in general an arbitrary function of *two* variables.

From (20) we may fall back on (18) by the consideration that in accordance with (10) μ' and a can occur only in the combination $\mu'a^n$.

It may be well to remark that the method of dimensions does not tell us whether or no an available solution can be deduced from particular assumptions. What it teaches us is the form which an available solution must assume. For example, equation (14) gives the form of the term in the virial proportional to v^{-1} , under the law of force (10); and nothing has been said as to any restriction upon the value of n . But it is easy to see that n must in fact be greater than 4. Otherwise the integral representing the virial relating to a given particle would not be convergent. We have to consider

$$\int \rho \phi(\rho) \rho^2 d\rho$$

with infinity for the upper limit, and this diverges unless n exceed 4.

It is not to be expected that any law included under (10) could represent with completeness the mutual action of the particles of a gas. Under it no provision can be made for repulsion at small distances and attraction at greater ones. And when $n > 4$, the aggregate virial depends too much upon the encounters which take place at exceedingly small distances.

If, as for both the virial terms in Van der Waals' formula, there be proportionality to v^{-1} , (20) becomes

$$\Sigma \rho \phi(\rho) = \frac{a^3 T}{v} F\left(\frac{\mu' a}{T}\right), \quad . \quad . \quad . \quad (21)$$

or, if we prefer it,

$$\Sigma \rho \phi(\rho) = \frac{\mu' a^4}{v} F\left(\frac{\mu' a}{T}\right), \quad . \quad . \quad . \quad (22)$$

F in both cases denoting an arbitrary function. According to Van der Waals F in (21) is a linear function, the constant part giving the collisional virial and the second term the cohesional virial which is independent of T . Except for one consideration to be mentioned presently, there would appear to be good reason for supposing the virial of a rare gas to be proportional to v^{-1} ; but on the other hand it is doubtful whether the cohesional forces are altogether of the kind supposed by Laplace and Van der Waals. We should expect the cohesional virial to be more directly influenced by the approaches of molecules during an encounter; and on the experimental side D. Berthelot has shown cause for preferring to that of Van der Waals the Rankine and Clausius

form, in which a factor T is introduced in the denominator. The most natural extension of the formula would be by substituting a quadratic for a linear form of F in (21). We should then write

$$\frac{1}{2}\Sigma\rho\phi(\rho)=\frac{3a^3}{2v}\left(-AT+B\mu'a+C\frac{\mu'^2a^2}{T}\right), \quad (23)$$

A, B, C being arbitrary constants ; and the pressure equation, when written after Van der Waals' manner with neglect of v^{-2} , becomes

$$\left\{p+\frac{a^3}{v^2}\left(B\mu'a+\frac{C\mu'^2a^2}{T}\right)\right\}\left\{v-\frac{a^3A}{R}\right\}=RT. \quad (24)$$

As has already been said, Van der Waals' form corresponds to $C=0$. On the other hand, the Rankine and Clausius form requires that $B=0$, while C remains finite. It will be evident that the two alternatives differ fundamentally. According to the latter the cohesive terms tend to vanish when T is sufficiently increased.

If the cohesive terms are to vanish when T is infinite, the forces concerned must be of an entirely different character from that contemplated in Laplace's and Van der Waals' theory. It has been suggested by Sutherland* that the forces may be of electric origin and in themselves (except during actual collision) as much repulsive as attractive. This is not inconsistent with the preponderance of attraction in the final result. "There is this fundamental distinction in the effects of attractive and repulsive forces whose strength decreases with increasing distance, that the attractive forces by their own operation tend to increase themselves, while the repulsive forces tend to decrease themselves." The forces contemplated by Sutherland are such as are due to electric or magnetic doublets, but a rather simpler illustration may be arrived at by retaining the single character of the centres of force, and supposing them to be as much positive as negative, under the usual electrical law that similars repel while opposites attract one another. When T is infinite, so that the paths are not influenced by the forces, the cohesive virial will disappear, but it may become finite as the temperature falls and room is given for the attractive forces to assert their advantage. There is nothing in the argument upon which (21) was founded which is interfered with by the occurrence of the two kinds of particles, and it would

* Phil. Mag. vol. iv. p. 625 (1902).

seem that F must then become an *even* function of μ' , so that in (23) $B=0$.

As stated, the above argument is probably not quite legitimate, inasmuch as according to (19) a reversal of μ' would imply a reversal of the collisional forces as well as of those which operate at greater distances. The introduction of the two sorts of particles is not supposed to alter the repulsive forces called into play during actual collision. I believe, however, that the instantaneous collisional forces may be omitted from (19). The effect of the collisions may be defined without reference to any datum having dimensions other than a , representing the radius of a sphere. The collisions being thus, as it were, already provided for, the argument remains that the virial must be a definite function of N, m, V, μ', a, v , of which N need not be regarded, the force (outside actual collision) being given by (19). Equation (21) then follows as before with its approximate form (23). If we now suppose that the particles are repellent as much as attractive, (19) may be written

$$\phi(\rho) = \pm \mu' f(\rho/a) ; \dots \dots \dots (25)$$

and, since odd powers of μ' are now excluded, $B=0$ in (23), (24).

We have thus discovered a possible theoretical foundation for the empirical conclusion that T should be introduced into the denominator of the cohesional virial, and it would seem to follow conversely that, if the empirical conclusion is correct, the forces must be intrinsically as much repellent as attractive. This argument may be regarded as a strong confirmation of Sutherland's idea, though a question remains as to how the attraction asserts its superiority over repulsion.

In the above argument the particles are regarded as simple centres of force, half of them being "positive" and half "negative." The advantage is that the form may still be treated as spherical, so that the collisions may be assimilated to those of "elastic spheres." But a polar constitution, such that the positive and negative elements are combined in every particle, is certainly more probable. This will introduce, as another linear datum, the distance between the poles, and the collisions will admit of greater variety. Moreover, there is now kinetic energy of rotation as well as of translation. However, since the kinetic energies are proportional, the argument remains unaffected, so far as it relates to the dependence of the virial of a given gas upon volume and temperature, and the Rankine-Clausius form (24) with $B=0$ still obtains.

As to the preponderance of attractive over repulsive virial, I think that the conclusion is correct, although Sutherland's argument, quoted above, omits reference to the essential consideration of the *time* for which any particular value of the virial prevails. If we fix our attention upon a pair of particles, acting as simple centres of force, which encounter one another, the corresponding virial varies from moment to moment, but the mean contribution to the total may be represented by

$$\int \phi(\rho) \rho dt,$$

the integration being taken over the whole range for which $\rho \phi(\rho)$ is sensible. Since only relative motion is in question, the centre of gravity of the two particles may be supposed to be at rest and the problem becomes one of "central forces." In the usual notation we have

$$\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 = P, \quad r^2 \frac{d\theta}{dt} = h, \quad . \quad . \quad . \quad (26)$$

so that

$$\begin{aligned} \int P.r.dt &= \left[r \frac{dr}{dt} \right] - \int \left(\frac{dr}{dt} \right)^2 dt - \int r^2 \left(\frac{d\theta}{dt} \right)^2 dt \\ &= \left[r \frac{dr}{dt} \right] - \int v^2 dt = \left[r \frac{dr}{dt} \right] - \int v ds, \quad . \quad (27) \end{aligned}$$

v denoting the resultant velocity. At the upper limit dr/dt is equal to the velocity at ∞ , say V , and at the lower limit $dr/dt = -V$. Hence

$$\int P.r.dt = 2rV - \int v ds, \quad . \quad . \quad . \quad (28)$$

so that the mean virial is closely connected with the "action" in the orbit.

For a simple illustration it will be more convenient to make θ the independent variable. Thus by (26)

$$\int P.r.dt = \frac{1}{h} \int P.r^3.d\theta. \quad . \quad . \quad . \quad (29)$$

Suppose for example that

$$P = \mu r^{-3} \quad . \quad . \quad . \quad (30)$$

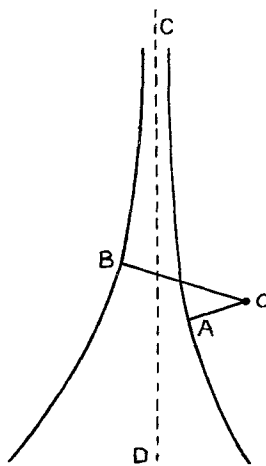
Then

$$\int P.r.dt = \frac{\mu}{h} \int d\theta = \frac{\mu}{h} \theta, \quad . \quad . \quad . \quad (31)$$

where θ represents twice the vectorial angle between the initial asymptote and the apse. If h be given, a comparison between repellent and attractive forces (μ given in magnitude but variable in sign) shows that (31) is greater in the case

of attraction (fig. 1), so that if attractive and repellent forces occur indifferently the average effect corresponds to attraction.

Fig. 1.



O, centre of force ; C D, asymptote ; A, B, apsides.

In the case of the particular law (30) we can carry out the calculation. If, as usual, $u=r^{-1}$, the equation of the orbit is

$$\frac{d^2u}{d\theta^2} + u = \frac{\mu}{h^2}u, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

μ being positive in the case of attraction ; whence, if μ be small,

$$u = U \sin \sqrt{(1 - \mu h^{-2})} \theta. \quad . \quad . \quad . \quad . \quad (33)$$

In (33) $u=0$, or $r=\infty$, when $\theta=0$ and when

$$\theta = \pi \div \sqrt{(1 - \mu h^{-2})} ; \quad . \quad . \quad . \quad . \quad (34)$$

so that from (31)

$$\int P.r.dt = \frac{\mu\pi}{\sqrt{(h^2 - \mu)}} \quad . \quad . \quad . \quad . \quad (35)$$

The solutions (33), (35) hold if μ be numerically less than h^2 , and (35) shows that when μ changes sign the virial of attraction preponderates. This conclusion is accentuated by the consideration of what occurs if μ exceed h^2 numerically. Equations (33), (35) still hold if μ be negative, *i. e.* if the force be repulsive. But when μ is positive, the form changes. Thus if $\mu=h^2$, we have

$$u = U\theta, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and neither θ in (31) nor the virial has a finite value. The like remains true when $\mu > h^2$.

In the above example Pr^3 remains constant, and the preponderance of attraction over repulsion depends upon the greater vectorial angle in the former case. If Pr^3 , instead of remaining constant, continually increases with diminishing r , the preponderance of attraction follows *a fortiori*.

A particular case of (32) which arises when $\mu = h^2$ should be singled out for especial notice, *i. e.* the case of circular motion for which $u = \text{constant}$. The attracting particles then revolve round one another in perpetuity, and the virial is infinite in comparison with that of an ordinary encounter. It is this possible occurrence of re-entrant orbits which causes hesitation as to the accuracy with which we may assume the virial of a rare gas to be inversely as the volume. It seems to be generally supposed (see, for example, Meyer's 'Kinetic Theory of Gases,' § 4) that if a gas be rare enough no appreciable pairing can occur. But the question is not as to the frequency with which new pairs may form, but as to the relative number of them in existence at any time. It is easy to recognize that the coupling or the severance of a pair of particles cannot occur of itself, but requires always the cooperation of a third particle. If the gas is very rare, no doubt there are few opportunities for the formation of fresh pairs, but for the same reason those already formed have a higher degree of permanence. On the whole it would appear that the number of pairs in existence at any moment is independent of the volume v of a rare gas, and the same would be true of the corresponding virial. At this rate we should have terms in the virial which by (20) come under the form

$$T \cdot F\left(\frac{\mu'a}{T}\right) \dots \dots \dots (37)$$

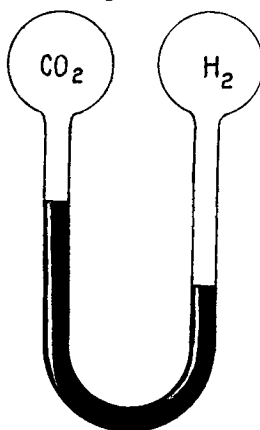
It will be remarked that if these terms in the virial, independent of v , are sensible, the density of the gas will depart from Avogadro's rule, however greatly it may be rarefied. In the case of elastic spheres, which come into collision when their centres approach to a certain distance, there is naturally a limit to the magnitude of the attraction, and then pairing becomes impossible if the velocity be sufficiently great. Any departure from Avogadro's rule at high rarefactions would thus tend to disappear as the temperature rises.

The behaviour of mere centres of force, which may approach one another without limit, appears to follow a different course. Taking for example the power law of (10),

we see from (18) that for any part of the virial which is independent of v , the function F must be constant, so that the virial is proportional to T and independent of μ .

To return to the question with which we started, there seems good reason to doubt that the relation of pressure to temperature with volume constant is accurately linear, even at high rarefactions. On the other hand, it is clear that this relation is approximately satisfied; and the natural course would be to take it as a foundation, determining the functions χ and ψ in (2), as well as the function of v and T jointly which may be required in supplement. As regards the latter part of the question, a differential arrangement in which two gases, say CO_2 and H_2 , are balanced against one another at the same temperature, would appear to offer advantages. This is shown diagrammatically in fig. 2, where the two gas-reservoirs are connected

Fig. 2.



by a U-tube containing mercury. According to Boyle's law, even as modified by the introduction of a co-volume, the mercury may stand in the U-tube at fixed marks at the *same level*, in spite of variations of temperature affecting both bulbs alike. And under the more general law (2) the same fixity of the mercury thread can be attained, though now with the extremities at different levels. With such an arrangement the departure from (2) becomes a matter of direct observation, and so long as *uniformity* of temperature is secured, a precise measurement of it, or of the *total* pressure, is of secondary importance. Useful results would probably require a total pressure of four or five atmospheres.

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