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XLII. On the momentum and pressure of gaseous vibrations, and on the connexion with the virial theorem

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XLII. On the Momentum and Pressure of Gaseous Vibrations, and on the Connexion with the Virial Theorem. By Lord RAYLEIGH, O.M., F.R.S.*

IN a paper on the Pressure of Vibrations (Phil. Mag. iii. p. 338, 1902) I considered the case of a gas obeying Boyle's law and vibrating within a cylinder in one dimension. It appeared that in consequence of the vibrations a piston closing the cylinder is subject to an additional pressure whose amount is measured by the volume-density of the total energy of vibration. More recently, in an interesting paper (Phil. Mag. ix. p. 393, 1905) Prof. Poynting has treated certain aspects of the question, especially the momentum associated with the propagation of progressive waves. Thus prompted, I have returned to the consideration of the subject, and have arrived at some more general results, which however do not in all respects fulfil the anticipations of Prof. Poynting. I commence with a calculation similar to that before given, but applicable to a gas in which the pressure is any arbitrary function of the density.

By the general hydrodynamical equation (Theory of Sound, § 253 *a*),

$$\varpi = \int \frac{dp}{\rho} = - \frac{d\phi}{dt} - \frac{1}{2}U^2 \dots \dots (1),$$

where p denotes the pressure, ρ the density, ϕ the velocity-potential, and U the resultant velocity at any point. If we integrate over a long period of time, ϕ disappears, and we see that

$$\int \varpi dt + \frac{1}{2} \int U^2 dt \dots \dots (2)$$

retains a constant value at all points of the cylinder. The value at the piston is accordingly the same as the mean value taken over the length of the cylinder.

If p_1, ρ_1 denote the pressure and density at the piston, and p_0, ρ_0 the pressure and density that would prevail throughout were there no vibrations, we have

$$p = f(\rho) = f(\rho_0 + \rho - \rho_0) \dots \dots (3),$$

and approximately

$$\begin{aligned} \varpi &= \int \rho^{-1} f'(\rho) d\rho = \int \frac{f'(\rho_0 + \rho - \rho_0)}{\rho_0 + \rho - \rho_0} d(\rho - \rho_0) \\ &= \frac{\rho - \rho_0}{\rho_0} f'(\rho_0) + \frac{(\rho - \rho_0)^2}{2\rho_0^2} \{ \rho_0 f''(\rho_0) - f'(\rho_0) \} \dots (4). \end{aligned}$$

* Communicated by the Author.

For the mean value of ϖ at the piston we have only to write ρ_1 for ρ in (4) and integrate with respect to t . And at the piston $U=0$.

For the mean of the whole length l of the cylinder (parallel to x), we have to integrate with respect to x as well as with respect to t . And in the integration with respect to x the first term of (4) disappears, inasmuch as the mean density remains the same as if there were no vibrations. Accordingly

$$f'(\rho_0) \int \frac{\rho_1 - \rho_0}{\rho_0} dt = \frac{1}{2} \iint \frac{U^2 dx dt}{l} + \{ \rho_0 f''(\rho_0) - f'(\rho_0) \} \left\{ \iint \frac{(\rho - \rho_0)^2 dx dt}{2\rho_0^2 l} - \int \frac{(\rho_1 - \rho_0)^2 dt}{2\rho_0^2} \right\} \quad (5),$$

the terms on the right being of the second order in the quantities which express the vibration.

Again,

$$\int (\rho_1 - \rho_0) dt = \int \{ f(\rho_1) - f(\rho_0) \} dt = \rho_0 f'(\rho_0) \int \frac{\rho_1 - \rho_0}{\rho_0} dt + \rho_0^2 f''(\rho_0) \int \frac{(\rho_1 - \rho_0)^2}{2\rho_0^2} dt ;$$

so that by (5)

$$\int (\rho_1 - \rho_0) dt = \frac{\rho_0}{2} \iint \frac{U^2 dx dt}{l} + \{ \rho_0^2 f''(\rho_0) - \rho_0 f'(\rho_0) \} \left\{ \iint \frac{(\rho - \rho_0)^2 dx dt}{2\rho_0^2 l} + \rho_0 f'(\rho_0) \int \frac{(\rho_1 - \rho_0)^2}{2\rho_0^2} dt \right\} \dots \dots (6).$$

The three integrals on the right in (6) are related in a way which we may deduce from the theory of infinitely small vibrations. If the velocity of propagation of such vibrations be denoted by a , then $f'(\rho_0) = a^2$. By the usual theory we have

$$U = \frac{d\phi}{dx}, \quad \frac{\rho - \rho_0}{\rho_0} = -\frac{1}{a^2} \frac{d\phi}{dt} \dots \dots (7).$$

If we suppose that the cylinder is closed at $x=0$ and at $x=l$, a normal vibration is expressed by

$$\phi = \cos \frac{s\pi x}{l} \cdot \cos \frac{s\pi at}{l} \dots \dots (8),$$

where s is any integer, giving

$$\frac{a^2}{2} \int \frac{(\rho_1 - \rho_0)^2}{\rho_0^2} dt = a^2 \iint \frac{(\rho - \rho_0)^2}{\rho_0^2} \frac{dx dt}{l} = \iint \frac{U^2 dx dt}{l} \quad (9),$$

the integrations with respect to x in (9) being taken from 0 to l , that is over the length of the cylinder.

The same conclusions (9) follow in the general case where ϕ is expressed by a sum of terms derived from (8) by attributing an integral value to s . The latter part expresses the equality of the mean potential and kinetic energies.

Introducing the relations (9) into (6), so as to express the mean pressure upon the piston in terms of the mean kinetic energy, we get as the final formula

$$\int (\rho_1 - \rho_0) dt = \left\{ \rho_0 + \frac{\rho_0^2 f''(\rho_0)}{2 f'(\rho_0)} \right\} \iint \frac{U^2 dx dt}{l} \quad (10).$$

Among special cases let us first take that of Boyle's law, where $p = a^2 \rho$, so that

$$f'(\rho_0) = a^2, \quad f''(\rho_0) = 0.$$

We have at once

$$\int (\rho_1 - \rho_0) dt = \rho_0 \iint \frac{U^2 dx dt}{l} \quad \dots \quad (11)$$

The expression on the right represents double the volume-density of the kinetic energy, or the volume-density of the whole energy, and we recover the result of the former investigation.

According to the adiabatic law

$$p/p_0 = (\rho/\rho_0)^\gamma \quad \dots \quad (12);$$

so that

$$f'(\rho_0) = \frac{p_0 \gamma}{\rho_0}, \quad f''(\rho_0) = \frac{p_0 \gamma (\gamma - 1)}{\rho_0^2} \quad \dots \quad (13).$$

Hence from (10)

$$\int (\rho_1 - \rho_0) dt = \frac{1}{2}(\gamma + 1) \rho_0 \iint \frac{U^2 dx dt}{l} \quad \dots \quad (14).$$

The mean pressure upon the piston is now $\frac{1}{2}(\gamma + 1)$ of the volume-density of the total energy. We fall back on Boyle's law by taking $\gamma = 1$.

It appears therefore that the result is altered when Boyle's law is departed from. Still more striking is the alteration when we take the case treated in 'Theory of Sound' § 250

of the law of pressure

$$p = \text{Const.} - a^2 \frac{\rho_0^2}{\rho} \quad \dots \quad (15).$$

According to this

$$f'(\rho_0) = a^2, \quad f''(\rho_0) = -2a^2/\rho_0 \quad \dots \quad (16),$$

and (10) gives

$$\int (p_1 - p_0) dt = 0 \quad \dots \quad (17).$$

The law of pressure (15) is that under which waves of finite condensation can be propagated without change of type.

In (17) the mean additional pressure vanishes, and the question arises whether it can be negative. It would appear so. If, for example,

$$p = \text{Const.} - \frac{a^2 \rho_0^3}{2\rho^2} \quad \dots \quad (18),$$

$$f'(\rho_0) = a^2, \quad f''(\rho_0) = -3a^2/\rho_0,$$

and

$$\int (p_1 - p_0) dt = -\frac{1}{2}\rho_0 \iint \frac{U^2 dx dt}{l} \quad \dots \quad (19).$$

I now pass on to the question of the *momentum* of a progressive train of waves. This question is connected with that already considered; for, as Prof. Poynting explains, if the reflexion of a train of waves exercises a pressure upon the reflector, it can only be because the train of waves itself involves momentum. From this argument we may infer already that momentum is not a necessary accompaniment of a train of waves. If the law were that of (15), no pressure would be exercised in reflexion. But it may be convenient to give a direct calculation of the momentum.

For this purpose we must know the relation which obtains in a progressive wave between the forward particle velocity u (not distinguished in one-dimensional motion from U) and the condensation $(\rho - \rho_0)/\rho_0$, usually denoted by s . When the disturbance is infinitely small, this relation is well known to be $u = as$, in the case of a positive wave. Thus

$$u : s = \sqrt{dp/d\rho} \quad \dots \quad (20).$$

The following is the method adopted in 'Theory of Sound,' § 351:—"If the above solution be violated at any point a wave will emerge, travelling in the negative direction. Let us now picture to ourselves the case of a positive progressive wave in which the changes of velocity and density are very gradual but become important by accumulation, and let us

inquire what conditions must be satisfied in order to prevent the formation of a negative wave. It is clear that the answer to the question whether, or not, a negative wave will be generated at any point will depend upon the state of things in the immediate neighbourhood of the point, and not upon the state of things at a distance from it, and will therefore be determined by the criterion applicable to small disturbances. In applying this criterion we are to consider the velocities and condensations not absolutely, but relatively, to those prevailing in the neighbouring parts of the medium, so that the form of (20) proper for the present purpose is

$$du = \sqrt{\left(\frac{dp}{d\rho}\right)} \cdot \frac{d\rho}{\rho} \quad \dots \quad (21),$$

whence

$$u = \int \sqrt{\left(\frac{dp}{d\rho}\right)} \cdot \frac{d\rho}{\rho} \quad \dots \quad (22),$$

which is the relation between u and ρ necessary for a positive progressive wave. Equation (22) was obtained analytically by Earnshaw (Phil. Trans. 1859, p. 146).

In the case of Boyle's law, $\sqrt{dp/d\rho}$ is constant, and the relation between velocity and density, given first, I believe, by Helmholtz, is

$$u = a \log (\rho/\rho_0),$$

if ρ_0 be the density corresponding to $u=0$."

In our previous notation

$$dp/d\rho = f'(\rho) = a^2 + f''(\rho_0) \cdot (\rho - \rho_0),$$

a being the velocity of infinitely small waves, equal to $\sqrt{\{f'(\rho_0)\}}$; and by (22)

$$u = a \frac{\rho - \rho_0}{\rho_0} + \frac{a}{\rho_0} \left(\frac{f''(\rho_0)}{2a^2} - \frac{1}{\rho_0} \right) \frac{(\rho - \rho_0)^2}{2} \quad \dots \quad (23),$$

the first term giving the usual approximate formula.

The momentum, reckoned per unit area of cross section,

$$= \int \rho u \, dx = \rho_0 \int \left(1 + \frac{\rho - \rho_0}{\rho_0} \right) u \, dx.$$

Introducing the value of u from (23) and assuming that the mean density is unaltered by the vibrations, we get

$$\rho_0 \left\{ \frac{\rho_0 f''(\rho_0)}{4a} + \frac{a}{2} \right\} \int \frac{(\rho - \rho_0)^2}{\rho_0^2} \, dx \quad \dots \quad (24),$$

or, if we prefer it,

$$\frac{\rho_0}{a^2} \left\{ \frac{\rho_0 f''(\rho_0)}{4a} + \frac{a}{2} \right\} \int u^2 dx \quad \dots \quad (25).$$

The total energy of the length considered is

$$\rho_0 \int u^2 dx ;$$

and the result may be thus stated

$$\text{momentum} = \left\{ \frac{\rho_0 f''(\rho_0)}{4a^3} + \frac{1}{2a} \right\} \times \text{total energy} \quad (26).$$

This may be compared with (10). If we suppose the long cylinder of length l to be occupied by a train of progressive waves moving towards the piston, the integrated pressure upon the piston during a time t , equal to l/a , should be equal to twice the momentum of the whole initial motion. The two formulæ are thus in accordance, and it is unnecessary to discuss (26) at length. It may suffice to call attention to Boyle's law, where $f''(\rho_0)=0$, and to the law of pressure (15) under which progressive waves have *no momentum*. It would seem that pressure and momentum are here associated with the tendency of waves to alter their form as they proceed on their course.

The above reasoning is perhaps as simple as could be expected; but an argument to be given later, relating to the kinetic theory of gases, led me to recognize, what is indeed tolerably obvious when once remarked, that there is here a close relation with the virial theorem of Clausius. If x, y, z be the coordinates; v_x, v_y, v_z the component velocities of a material particle of mass m , then

$$\frac{1}{2} \sum m v_x^2 = -\frac{1}{2} \sum Xx + \frac{1}{4} \frac{d^2 \sum m x^2}{dt^2}$$

with two similar equations, X being the impressed force in the direction of x operative upon m . If the motion be what is called stationary, and if we understand the symbols to represent always the mean values with respect to time, the last term disappears, and

$$\frac{1}{2} \sum m v_x^2 = -\frac{1}{2} \sum Xx \quad \dots \quad (27).$$

The mean kinetic energy of the system relative to any direction is equal to the virial relative to the same direction.

Let us apply (27) to our problem of the one-dimensional motion of a gas within a cylinder provided with closed ends.

As in other applications of the virial theorem, the forces X are divided into two groups, internal and external. The latter reduces to the forces between the ends (pistons) and the gas. If p_1 be the pressure on the pistons—it will be the same on the average at both ends—the external virial is per unit of area $\frac{1}{2}p_1l$ simply. As regards the internal virial, I do not remember to have seen its value stated, probably because in hydrodynamics the mechanical properties of a fluid are not usually traced to forces acting between the particles. There can be no doubt, however, what the value is. If we suppose that the whole mass of gas in (27) is at rest, the left-hand member vanishes, so that the sum of the internal and external virial must vanish. Under a uniform pressure p_0 , the internal virial is therefore $\frac{1}{2}p_0l$. In an actual gas the virial for any part can depend only on the local density, so that whether the gas be in motion or not, the value of the internal virial is

$$-\frac{1}{2} \int_0^l p \, dx \quad . \quad . \quad . \quad . \quad . \quad (28).$$

Hence (27) gives

$$\begin{aligned} \text{kinetic energy} &= \frac{1}{2}p_1l - \frac{1}{2} \int_0^l p \, dx \\ &= \frac{1}{2}(p_1 - p_0)l - \frac{1}{2} \int_0^l (p - p_0) \, dx \quad . \quad (29). \end{aligned}$$

If the gas be subject to Boyle's law, pressure is proportional to density, and the last term in (29) disappears. The additional pressure on the ends ($p_1 - p_0$) is thus equal to twice the density of the kinetic energy.

In general,

$$p - p_0 = a^2(\rho - \rho_0) + \frac{1}{2}f''(\rho_0) \cdot (\rho - \rho_0)^2,$$

and

$$\int_0^l (p - p_0) \, dx = \frac{1}{2}f''(\rho_0) \int (\rho - \rho_0)^2 \, dx.$$

If we introduce expressly the integration with respect to t already implied, (29) gives

$$\begin{aligned} l \int (p_1 - p_0) \, dt &= \rho_0 \iint U^2 \, dx \, dt + \frac{1}{2}f''(\rho_0) \iint (\rho - \rho_0)^2 \, dx \, dt \\ &= \left\{ \rho_0 + \frac{\rho_0^2 f''(\rho_0)}{2a^2} \right\} \iint U^2 \, dx \, dt, \end{aligned}$$

regard being paid to (9). Equation (10) is thus derived very simply from the virial.

In all that precedes, the motion of the gas has been in one dimension, and even when we supposed the gas to be confined in a cylinder, we were able to avoid the consideration of lateral pressures upon the walls of the cylinder by applying the virial equation in its one-dimensional form. We now pass on to the case of three dimensions, and the first question which arises is as to the value of the virial. In place of (27) we have now

$$\frac{1}{2} \Sigma m U^2 = -\frac{1}{2} \Sigma (Xx + Yy + Zz) . . . (30),$$

U being the resultant velocity, Y, Z impressed forces parallel to the axes of *y* and *z*. Let us first apply this to a gas at rest under pressure p_0 . The total virial, represented by the right-hand member of (30), is now zero; that is, the internal and external virial balance one another. As is well known and as we may verify at once by considering the case of a rectangular chamber, the external virial is $\frac{3}{2} p_0 v$, *v* denoting the volume of gas. The internal virial is accordingly $-\frac{3}{2} p_0 v$; and from this we may infer that whether the pressure be uniform or not, the internal virial is expressed by

$$-\frac{3}{2} \iiint p \, dx \, dy \, dz, (31).$$

The difference between the internal virial of the gas in motion and in equilibrium is

$$-\frac{3}{2} \iiint (p - p_0) \, dx \, dy \, dz (31 *).$$

According to the law of Boyle, (31*) must vanish, since the mean density of the whole mass cannot be altered. The internal virial is therefore the same whether the gas be at rest or in motion.

A question arises here as to whether a particular law of pressure may not be fundamentally inconsistent with the statical Boscovitchian theory of the constitution of a gas upon which the application of the virial theorem is based. If, indeed, we assume Boyle's law in its integrity, the inconsistency does exist. For Maxwell has shown (Scientific Papers, vol. ii. p. 422) that on a statical theory Boyle's law involves between the molecules of a gas a repulsion inversely as the distance. This makes the internal virial for any pair of molecules independent of their mutual distance, and thus the virial for the whole mass independent of the distribution of the parts. But such an explanation of Boyle's law violates the principle upon which (31) was deduced, making the pressure dependent upon the total quantity of the mass and not merely upon the local density; from which

Maxwell concluded that all statical theories are to be rejected. It is to be remarked, however, that our calculations involve the law of pressure only as far as the term involving the square of the variation of density, and that a law agreeing with Boyle's to this degree of approximation may perhaps not be inconsistent with a statical Boscovitchian theory*.

Passing over this point, we find in general from (30)

$$\frac{1}{2} \Sigma m U^2 = \frac{3}{2} (p_1 - p_0) v - \frac{3}{2} \iiint (p - p_0) dx dy dz . \quad (32),$$

whenever the character of the motion is such that the mean pressure (p_1) is the same at all points of the walls of the chamber. Further, as before,

$$\iiint (p - p_0) dx dy dz = \frac{1}{2} f''(\rho_0) \iiint (\rho - \rho_0)^2 dx dy dz,$$

and finally, regard being paid to (9) as extended to three dimensions,

$$(p_1 - p_0) v = \left(\frac{1}{3} + \frac{\rho_0 f''(\rho_0)}{2a^2} \right) \times \text{total energy} . \quad (33).$$

In the case of Boyle's law $f'' = 0$, and we see that the mean pressure upon the walls of the chamber is measured by one-third of the volume-density of the total energy.

For the adiabatic law (12), (13) gives

$$(p_1 - p_0) v = \left(\frac{1}{3} + \frac{\gamma - 1}{2} \right) \times \text{total energy} . \quad (34).$$

In the case of certain gases called *monatomic*, $\gamma = 1\frac{2}{3}$, and (34) becomes

$$(p_1 - p_0) v = \frac{2}{3} \times \text{total energy} . . . \quad (35).$$

Thirdly, in the case of the law (15) for the relation between pressure and density,

$$(p_1 - p_0) v = -\frac{2}{3} \times \text{total energy} . . . \quad (36),$$

the mean pressure upon the walls being *less* than if there were no motion.

So far we have treated the question on the usual hydrodynamical basis, reckoning the energy of compression or

* I think the difficulty may be turned by supposing the force, inversely as the distance, to operate only between particles whose mutual distance is small, and that outside a certain small distance the force is zero. All that is necessary is that a pair of particles once within the range of the force should always remain within it—a condition easily satisfied so long as small disturbances alone are considered.

rarefaction as *potential*. It was, however, on the lines of the kinetic theory that I first applied the virial theorem to the question of the pressure of vibrations. In the form of this theory which regards the collisions of molecules as instantaneous, there is practically no potential, but only kinetic energy. And if the gas be monatomic, the whole of this energy is translational. If V be the resultant velocity of the molecule whose mass is m , the virial equation gives

$$\frac{3}{2}p_1v = \frac{1}{2}\Sigma mV^2 \quad . \quad . \quad . \quad (37),$$

p_1 denoting, as before, the pressure upon the walls, assumed to be the same over the whole area. If necessary, p_1 and ΣmV^2 are to be averaged with respect to time.

It is usually to a gas in equilibrium that (37) is applied, but this restriction is not necessary. Whether there be vibrations or not, p_1 is equal to $\frac{2}{3}$ of the volume-density of the whole energy of the molecules. Consider a given chamber whose walls are perfectly reflecting, and let it be occupied by a gas in equilibrium. The pressure is given by (37). Suppose now that additional energy (which can only be kinetic) is communicated. We learn from (37) that the additional pressure is measured by $\frac{2}{3}$ of the volume-density of the additional energy, whether this additional energy be in the form of heat, equally or unequally distributed, or whether it take the form of mechanical vibrations, *i. e.* of coordinated velocities and density differences. Under the influence of heat-conduction and viscosity the mechanical vibrations gradually die down, but the pressure undergoes no change.

The above is the case of the adiabatic law with $\gamma = 1\frac{2}{3}$ already considered in (35), and a comparison of the two methods of treatment, in one of which potential energy plays a large part, while in the other all the energy is regarded as kinetic, suggests interesting reflexions as to what is really involved in the distinction of the two kinds of energy.

If we abandon the restriction to monatomic molecules, the question naturally becomes more complicated. We have first to consider in what form the virial equation should be stated. In the case of a diatomic molecule we have, in the first instance, not only the kinetic energy of the molecule as a whole, but also the kinetic energy of rotation, and in addition the internal virial of the force by which the union of the two atoms is maintained. It is easy to see, however, that the two latter terms balance one another, so that we are left with the kinetic energy of the molecule as a whole. For

general purposes a theorem is required of which I have not met a complete statement. For any part of a wider system for which we wish to form the virial equation, we may omit the kinetic energy of the motion relative to the centre of gravity of the part, if at the same time we omit the virial of the internal forces operative in this part and treat the forces acting from outside upon the part, whether from the remainder of the system or wholly from outside, as acting at the centre of gravity of the part. In applying (37) to a gas regarded as composed of molecules, we are therefore to include on the right only the kinetic energy of translation of the molecules. If a gas originally at rest be set into vibration, we have

$$\frac{3}{2}(p_1 - p_0)v = \text{additional energy of translation.} \quad (38).$$

The pressure p_1 does not now, as in the case of monatomic gases, remain constant. Under the influence of viscosity and heat-conduction, part of the energy at first translational becomes converted into other forms.

A complete discussion here would carry us into the inner shrine of the kinetic theory. We will only pursue the subject so far as to consider briefly the case of rigid molecules for which the energy is still entirely kinetic—partly that of the translatory motion of the molecules as wholes and partly rotatory. Of the additional energy E representing the vibrations, half may be regarded as wholly translational. Of the other half, the fraction which is translational is $3/m$, where m is the whole number of modes. The translational part of E is therefore $\frac{1}{2}E(1 + 3/m)$; so that

$$(p_1 - p_0)v = E \left(\frac{1}{3} + \frac{1}{m} \right) \dots \dots (39).$$

If $m = 3$, as for monatomic molecules, we recover the former result; otherwise $p_1 - p_0$ is less. In terms of γ we have

$$\gamma = 1 + 2/m \dots \dots (40),$$

and accordingly

$$(p_1 - p_0)v = E \left(\frac{1}{3} - \frac{\gamma - 1}{2} \right) \dots \dots (41),$$

in agreement with (34) where what was there called the total energy is now regarded as the additional energy of vibration. In the case of a diatomic gas, $m = 5$, $\gamma = 1\frac{2}{5}$.

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July 26.