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XXXIV. *On the Theory of Surface Forces.* *By* Lord RAYLEIGH, *Sec. R.S.**

SINCE the time of Young the tendency of a liquid surface to contract has always been attributed to the mutual attraction of the parts of the liquid, acting through a very small range,—to the same forces in fact as those by which the cohesion of liquids and solids is to be explained. It is sometimes asserted that Laplace was the first to look at the matter from this point of view, and that Young contented himself with calculations of the *consequences* of superficial tension. Such an opinion is entirely mistaken, although the authority of Laplace himself may be quoted in its favour†. In the introduction to his first paper‡, which preceded the work of Laplace, Young writes :—"It will perhaps be more agreeable to the experimental philosopher, although less consistent with the strict course of logical argument, to proceed in the first place to the comparison of this theory [of superficial tension] with the phenomena, and to inquire afterwards for its foundation in the ultimate properties of matter." This he attempts to do in Section VI., which is headed *Physical Foundation of*

* Communicated by the Author.

† *Méc. Cél. Supplément au* X^{e} *livre*, 1805:—"Mais il n'a pas tenté, comme Segner, de dériver ces hypothèses, de la loi de l'attraction des molécules, decroissante avec une extrême rapidité; ce qui était indispensable pour les réaliser."

‡ "On the Cohesion of Fluids," Phil. Trans. 1805.

the Law of Superficial Cohesion. The argument is certainly somewhat obscure; but as to the character of the "physical foundation" there can be no doubt. "We may suppose the particles of liquids, and probably those of solids also, to possess that power of repulsion, which has been demonstrably shown by Newton to exist in aëriform fluids, and which varies in the inverse ratio of the distance of the particles from each other. In air and vapours this force appears to act uncontrolled; but in liquids it is overcome by a cohesive force, while the particles still retain a power of moving freely in all directions..... It is simplest to suppose the force of cohesion nearly or perfectly constant in its magnitude, throughout the minute distance to which it extends, and owing its apparent diversity to the contrary action of the repulsive force which varies with the distance."

Although nearly a century has elapsed, we are still far from a satisfactory theory of these reactions. We know now that the pressure of gases cannot be explained by a repulsive force varying inversely as the distance, but that we must appeal to the impacts of colliding molecules *. There is every reason to suppose that the molecular movements play an important part in liquids also; and if we leave them out of account, we can only excuse ourselves on the ground of the difficulty of the subject, and with full recognition that a theory so founded is probably only a first approximation to the truth. On the other hand, the progress of science has tended to confirm the views of Young and Laplace as to the existence of a powerful attraction operative at short distances. Even in the theory of gases it is necessary, as Van der Waals has shown, to appeal to such a force in order to explain their condensation under increasing pressure in excess of that indicated by Boyle's law, and explicable by impacts. Again, it would appear that it is in order to overcome this attraction that so much heat is required in the evaporation of liquids.

If we take a statical view of the matter, and ignore the molecular movements †, we must introduce a repulsive force to compensate the attraction. Upon this point there has been a good deal of confusion, of which even Poisson cannot be acquitted. And yet the case seems simple enough. For consider the equilibrium of a spherical mass of mutually attracting matter, free from external force, and conceive it divided by

* The argument is clearly set forth in Maxwell's lecture "On the Dynamical Evidence of the Molecular Constitution of Bodies" (Nature, vol. xi. p. 357, 1875).

† Compare Worthington, "On Surface Forces in Fluids," Phil. Mag. xviii. p. 334 (1884).

an ideal plane into hemispheres. Since the hemispheres are at rest, their total action upon one another must be zero, that is, no force is transmitted across the interface. If there be attraction operative across the interface, it must be precisely compensated by repulsion. This view of the matter was from the first familiar to Young, and he afterwards gave calculations, which we shall presently notice, dependent upon the hypothesis that there is a constant attractive force operative over a limited range and balanced by a repulsive force of suitable intensity operative over a different range. In Laplace's theory, upon the other hand, no mention is made of repulsive forces, and it would appear at first as if the attractive forces were left to perform the impossible feat of balancing themselves. But in this theory there is introduced a pressure which is really the representative of the repulsive forces.

It may be objected that if the attraction and repulsion must be supposed to balance one another across any ideal plane of separation, there can be no sense, or advantage, in admitting the existence of either. This would certainly be true if the origin and law of action of the forces were similar, but such is not supposed to be the case. The inconclusiveness of the objection is readily illustrated. Consider the case of the earth, conceived to be at rest. The two halves into which it may be divided by an ideal plane do not upon the whole act upon one another; otherwise there could not be equilibrium. Nevertheless no one hesitates to say that the two halves attract one another under the law of gravitation. The force of the objection is sometimes directed against the pressure, denoted by K, which Laplace conceives to prevail in the interior of liquids and solids. How, it is asked, can there be a pressure, if the whole force vanishes? The best answer to this question may be found in asking another—Is there a pressure in the interior of the earth?

It must no doubt be admitted that in availing ourselves of the conception of pressure we are stopping short of a complete explanation. The mechanism of the pressure is one of the things that we should like to understand. But Laplace's theory, while ignoring the movements and even the existence of molecules, cannot profess to be complete; and there seems to be no inconsistency in the conception of a continuous, incompressible liquid, whose parts attract one another, but are prevented from undergoing condensation by forces of infinitely small range, into the nature of which we do not further inquire. All that we need to take into account is then covered by the ordinary idea of pressure. However imperfect a theory developed on these lines may be, and indeed must be, it presents to the mind a good picture of capillary phenomena, and, as it probably contains nothing not needed for the further development of the subject, labour spent upon it can hardly be thrown away.

Upon this view the pressure due to the attraction measures the cohesive force of the substance, that is the tension which must be applied in order to cause rupture. It is the quantity which Laplace denoted by K, and which is often called the molecular pressure. Inasmuch as Laplace's theory is not a molecular theory at all, this name does not seem very appropriate. Intrinsic pressure is perhaps a better term, and will be employed here. The simplest method of estimating the intrinsic pressure is by the force required to break solids. As to liquids, it is often supposed that the smallest force is adequate to tear them asunder. If this were true, the theory of capillarity now under consideration would be upset from its foundations, but the fact is quite otherwise. Berthelot* found that water could sustain a tension of about 50 atmospheres applied directly, and the well-known phenomenon of retarded ebullition points in the same direction. For if the cohesive forces which tend to close up a small cavity in the interior of a superheated liquid were less powerful than the steam-pressure, the cavity must expand, that is the liquid must boil. By supposing the cavity infinitely small, we see that ebullition must necessarily set in as soon as the steam † pressure exceeds that intrinsic to the liquid. The same method may be applied to form a conception of the intrinsic pressure of a liquid which is not superheated. The walls of a moderately small cavity certainly tend to collapse with a force measured by the constant surface-tension of the liquid. The pressure in the cavity is at first proportional to the surface-tension and to the curvature of the walls. If this law held without limit, the consideration of an infinitely small cavity shows that the intrinsic pressure would be infinite in all liquids. Of course the law really changes when the dimensions of the cavity are of the same order as the range of the attractive forces, and the pressure in the cavity approaches a limit, which is the intrinsic pressure of the liquid. In this way we are forced to admit the reality of the pressure by the consideration of experimental facts which cannot be disputed.

The first estimate of the intrinsic pressure of water is doubtless that of Young. It is 23,000 atmospheres, and agrees

* *Ann. de Chimie*, xxx. p. 232 (1850). See also Worthington, Brit. Assoc. Report, 1888, p. 583.

† If there be any more volatile impurity (*e.g.* dissolved gas) ebullition must occur much earlier.

extraordinarily well with modern numbers. I propose to return to this estimate, and to the remarkable argument which Young founded upon it.

The first great advance upon the theory of Young and Laplace was the establishment by Gauss of the principle of surface-energy. He observed that the existence of attractive forces of the kind supposed by his predecessors leads of necessity to a term in the expression of the potential energy proportional to the surface of the liquid, so that a liquid surface tends always to contract, or, what means precisely the same thing, exercises a tension. The argument has been put into a more general form by Boltzmann*. It is clear that all molecules in the interior of the liquid are in the same condition. Within the superficial layer, considered to be of finite but very small thickness, the condition of all molecules is the same which lie at the same very small distance from the surface. If the liquid be deformed without change in the total area of the surface, the potential energy necessarily remains unaltered; but if there be a change of area the variation of potential energy must be proportional to such change.

A mass of liquid, left to the sole action of cohesive forces, assumes a spherical figure. We may usefully interpret this as a tendency of the surface to contract; but it is important not to lose sight of the idea that the spherical form is the result of the endeavour of the parts to get *as near to one another* as is possible†. A drop is spherical under capillary forces for the same reason that a large gravitating mass of (non-rotating) liquid is spherical.

In the following sketch of Laplace's theory we will commence in the manner adopted by Maxwell‡. If f be the distance between two particles m, m', the cohesive attraction between them is denoted in Laplace's notation by $m m' \phi(f)$, where $\phi(f)$ is a function of f which is insensible for all sensible values of f, but which becomes sensible and even enormously great, when f is exceedingly small.

"If we next introduce a new function of f and write

$$\int_f^\infty \phi(f)\, df = \Pi(f), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

then $m m' \Pi(f)$ will represent (1) the work done by the

* Pogg. *Ann.* cxli. p. 582 (1870). See also Maxwell's 'Theory of Heat,' 1870; and article "Capillarity," *Enc. Brit.*

† See Sir W. Thomson's lecture on Capillary Attraction (Proc. Roy Inst. 1886), reprinted in 'Popular Lectures and Addresses.'

‡ *Enc. Brit.*, "Capillarity."

attractive force on the particle m, while it is brought from an infinite distance from m' to the distance f from m'; or (2) the attraction of a particle m on a narrow straight rod resolved in the direction of the length of the rod, one extremity of the rod being at a distance f from m, and the other at an infinite distance, the mass of unit of length of the rod being m'. The function $\Pi(f)$ is also insensible for sensible values of f, but for insensible values of f it may become sensible and even very great."

"If we next write

$$\int_z^\infty \Pi(f) f\, df = \psi(z), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

then $2\pi m\sigma\psi(z)$ will represent (1) the work done by the attractive force while a particle m is brought from an infinite distance to a distance z from an infinitely thin stratum of the substance whose mass per unit of area is σ; (2) the attraction of a particle m placed at a distance z from the plane surface of an infinite solid whose density is σ."

The intrinsic pressure can now be found immediately by calculating the mutual attraction of the parts of a large mass which lie on opposite sides of an imaginary plane interface. If the density be σ, the attraction between the whole of one side and a layer upon the other distant z from the plane and of thickness dz is $2\pi\sigma^2\psi(z)\,dz$, reckoned per unit of area. The expression for the intrinsic pressure is thus simply

$$\mathrm{K} = 2\pi\,\sigma^2 \int_0^\infty \psi(z)\,dz. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In Laplace's investigation σ is supposed to be unity. We may call the value which (3) then assumes K_0, so that

$$\mathrm{K}_0 = 2\pi \int_0^\infty \psi(z)\,dz. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The expression for the superficial tension is most readily found with the aid of the idea of superficial energy, introduced into the subject by Gauss. Since the tension is constant, the work that must be done to extend the surface by one unit of area measures the tension, and the work required for the generation of any surface is the product of the tension and the area. From this consideration we may derive Laplace's expression, as has been done by Dupré* and Thomson†. For imagine a small cavity to be formed in the interior of the

* *Théorie Mécanique de la Chaleur* (Paris, 1869).

† "Capillary Attraction," Proc. Roy. Inst. Jan. 1886. Reprinted, 'Popular Lectures and Addresses,' 1889.

mass and to be gradually expanded in such a shape that the walls consist almost entirely of two parallel planes. The distance between the planes is supposed to be very small compared with their ultimate diameters, but at the same time large enough to exceed the range of the attractive forces. The work required to produce this crevasse is twice the product of the tension and the area of one of the faces. If we now suppose the crevasse produced by direct separation of its walls, the work necessary must be the same as before, the initial and final configurations being identical; and we recognize that the tension may be measured by half the work that must be done per unit of area against the mutual attraction in order to separate the two portions which lie upon opposite sides of an ideal plane to a distance from one another which is outside the range of the forces. It only remains to calculate this work.

If σ_1, σ_2 represent the densities of the two infinite solids, their mutual attraction at distance z is per unit of area

$$2\pi\sigma_1\sigma_2\int_z^\infty \psi(z)\,dz, \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

or $2\pi\sigma_1\sigma_2\,\theta(z)$, if we write

$$\int_z^\infty \psi(z)\,dz=\theta(z). \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

The work required to produce the separation in question is thus

$$2\pi\sigma_1\sigma_2\int_0^\infty \theta(z)\,dz; \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

and for the tension of a liquid of density σ we have

$$\mathrm{T}=\pi\sigma^2\int_0^\infty \theta(z)\,dz. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

The form of this expression may be modified by integration by parts. For

$$\int\theta(z)\,dz=\theta(z)\,.\,z-\int z\,\frac{d\theta(z)}{dz}\,dz=\theta(z)\,.\,z+\int z\,\psi(z)\,dz.$$

Since $\theta(0)$ is finite, proportional to K, the integrated term vanishes at both limits, and we have simply

$$\int_0^\infty \theta(z)\,dz=\int_0^\infty z\,\psi(z)\,dz, \quad . \quad . \quad . \quad . \qquad (9)$$

and

$$\mathrm{T}=\pi\sigma^2\int_0^\infty z\,\psi(z)\,dz. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

In Laplace's notation the second member of (9), multiplied by 2π, is represented by H.

As Laplace has shown, the values for K and T may also be expressed in terms of the function ϕ, with which we started. Integrating by parts, we get by means of (1) and (2),

$$\int \psi(z)\, dz = z\,\psi(z) + \tfrac{1}{3} z^3 \Pi(z) + \tfrac{1}{3}\int z^3 \phi(z)\, dz,$$

$$\int z\,\psi(z)\, dz = \tfrac{1}{2} z^2 \psi(z) + \tfrac{1}{8} z^4 \Pi(z) + \tfrac{1}{8}\int z^4 \phi(z)\, dz.$$

In all cases to which it is necessary to have regard the integrated terms vanish at both limits, and we may write

$$\int_0^\infty \psi(z)\, dz = \tfrac{1}{3}\int_0^\infty z^3\phi(z)\, dz, \quad \int_0^\infty z\,\psi(z)\, dz = \tfrac{1}{8}\int_0^\infty z^4 \phi(z)\, dz; \quad (11)$$

so that

$$K_0 = \frac{2\pi}{3}\int_0^\infty z^3 \phi(z)\, dz, \qquad T_0 = \frac{\pi}{8}\int_0^\infty z^4\phi(z)\, dz. \quad (12)$$

A few examples of these formulæ will promote an intelligent comprehension of the subject. One of the simplest suppositions open to us is that

$$\phi(f) = e^{-\beta f}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

From this we obtain

$$\Pi(z) = \beta^{-1} e^{-\beta z}, \quad \psi(z) = \beta^{-3}(\beta z + 1) e^{-\beta z}, \quad . \quad (14)$$

$$K_0 = 4\pi\beta^{-4}, \qquad T_0 = 3\pi\beta^{-5}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The range of the attractive force is mathematically infinite, but practically of the order β^{-1}, and we see that T is of higher order in this small quantity than K. That K is in all cases of the fourth order and T of the fifth order in the range of the forces is obvious from (12) without integration.

An apparently simple example would be to suppose $\phi(z) = z^n$. From (1), (2), (4) we get

$$\Pi(z) = -\frac{z^{n+1}}{n+1}, \quad \psi(z) = \frac{z^{n+3}}{n+3\,.\,n+1},$$

$$K_0 = \left.\frac{2\pi z^{n+4}}{n+4\,.\,n+3\,.\,n+1}\right|_0^\infty. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The intrinsic pressure will thus be infinite whatever n may be. If $n+4$ be positive, the attraction of infinitely distant parts contributes to the result; while if $n+4$ be negative, the parts in immediate contiguity act with infinite power. For the transition case, discussed by Sutherland*, of $n+4=0$,

* Phil. Mag. xxiv. p. 113 (1887).

K_0 is also infinite. It seems therefore that nothing satisfactory can be arrived at under this head.

As a third example we will take the law proposed by Young, viz.

$$\left.\begin{array}{l}\phi(z)=1 \text{ from } z=0 \text{ to } z=a,\\ \phi(z)=0 \text{ from } z=a \text{ to } z=\infty\,;\end{array}\right\} \quad . \quad . \quad . \quad (17)$$

and corresponding therewith,

$$\left.\begin{array}{ll}\Pi(z)=a-z & \text{from } z=0 \text{ to } z=a,\\ \Pi(z)=0 & \text{from } z=a \text{ to } z=\infty,\end{array}\right\} \quad . \quad . \quad (18)$$

$$\left.\begin{array}{ll}\psi(z)=\tfrac{1}{2}a(a^2-z^2)-\tfrac{1}{3}(a^3-z^3) & \\ & \text{from } z=0 \text{ to } z=a,\\ \psi(z)=0 & \text{from } z=a \text{ to } z=\infty.\end{array}\right\} \quad . \quad . \quad (19)$$

Equations (12) now give

$$K_0=\frac{2\pi}{3}\int_0^\infty z^3\,dz=\frac{\pi a^4}{6}, \quad . \quad . \quad . \quad . \quad (20)$$

$$T_0=\frac{\pi}{8}\int_0^a z^4\,dz=\frac{\pi a^5}{40}. \quad . \quad . \quad . \quad . \quad (21)$$

The numerical results differ from those of Young*, who finds that "*the contractile force is one-third of the whole cohesive force of a stratum of particles, equal in thickness to the interval to which the primitive equable cohesion extends,*" viz. $T=\frac{1}{3}aK$; whereas according to the above calculation $T=\frac{3}{20}aK$. The discrepancy seems to depend upon Young having treated the attractive force as operative in one direction only.

In his Elementary Illustrations of the Celestial Mechanics of Laplace†, Young expresses views not in all respects consistent with those of his earlier papers. In order to balance the attractive force he introduces a repulsive force, following the same law as the attractive except as to the magnitude of the range. The attraction is supposed to be of constant intensity C over a range c, while the repulsion is of intensity R, and is operative over a range r. The calculation above given is still applicable, and we find that

$$\left.\begin{array}{l}K=\dfrac{\pi}{6}(c^4C-r^4R),\\[2ex] T=\dfrac{\pi}{40}(c^5C-r^5R).\end{array}\right\} \quad . \quad . \quad . \quad . \quad (22)$$

* *Enc. Brit.*; Collected Works, vol. i. p. 461.

† 1821. Collected Works, vol. i. p. 485.

In these equations, however, we are to treat K as vanishing, the specification of the forces operative across a plane being supposed to be complete. Hence, as Young finds, we must take

$$c^4\mathrm{C}=r^4\mathrm{R}\,; \qquad \ldots \ldots \qquad (23)$$

and accordingly

$$\mathrm{T}=\frac{\pi c^4\mathrm{C}(c-r)}{40}. \qquad \ldots \ldots \qquad (24)$$

At this point I am not able to follow Young's argument, for he asserts (p. 490) that "the existence of such a cohesive tension proves that the mean sphere of action of the repulsive force is more extended than that of the cohesive: a conclusion which, though contrary to the tendency of some other modes of viewing the subject, shows the absolute insufficiency of all theories built upon the examination of one kind of corpuscular force alone." According to (24) we should infer, on the contrary, that if superficial tension is to be explained in this way, we must suppose that $c > r$.

My own impression is that we do not gain anything by this attempt to advance beyond the position of Laplace. So long as we are content to treat fluids as incompressible there is no objection to the conception of intrinsic pressure. The repulsive forces which constitute the machinery of this pressure are probably intimately associated with actual compression, and cannot advantageously be treated without enlarging the foundations of the theory. Indeed it seems that the view of the subject represented by (23), (24), with c greater than r, cannot consistently be maintained. For consider the equilibrium of a layer of liquid at a free surface A of thickness AB equal to r. If the void space beyond A were filled up with liquid, the attractions and repulsions across B would balance one another; and since the action of the additional liquid upon the parts below B is wholly attractive, it is clear that in the actual state of things there is a finite repulsive action across B, and a consequent failure of equilibrium.

I now propose to exhibit another method of calculation, which not only leads more directly to the results of Laplace, but allows us to make a not unimportant extension of the formulæ to meet the case where the radius of a spherical cavity is neither very large nor very small in comparison with the range of the forces.

The density of the fluid being taken as unity, let V be the potential of the attraction, so that

$$\mathrm{V}=\iiint \Pi(f)\,dx\,dy\,dz, \qquad \ldots \ldots \qquad (25)$$

f denoting the distance of the element of the fluid $dx\,dy\,dz$ from the point at which the potential is to be reckoned. The hydrostatic equation of pressure is then simply

$$dp = dV\ ;$$

or, if A and B be any two points,

$$p_B - p_A = V_B - V_A. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Suppose, for example, that A is in the interior, and B upon a plane surface of the liquid. The potential at B is then exactly one half of that at A, or $V_B = \frac{1}{2} V_A$; so that

$$p_A - p_B = \tfrac{1}{2} V_A = 2\pi \int_0^{\frac{1}{2}\pi} \int_0^{\infty} \Pi(f) f^2\, df \sin\theta\, d\theta$$

$$= 2\pi \int_0^{\infty} \Pi(f) f^2\, df.$$

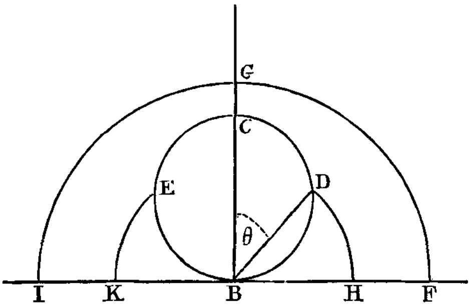
Now $p_A - p_B$ is the intrinsic pressure K_0; and thus

$$K_0 = 2\pi \int_0^{\infty} \Pi(f) f^2\, df = \frac{2\pi}{3} \int_0^{\infty} \phi(f) f^3\, df,$$

as before.

Again, let us suppose that the fluid is bounded by concentric spherical surfaces, the interior one of radius r being either large or small, but the exterior one so large that its curvature may be neglected. We may suppose that there is no external pressure, and that the tendency of the cavity to collapse is balanced by contained gas. Our object is to estimate the necessary internal pressure.

Fig. 1.



In the figure B D C E represents the cavity, and the pressure required is the same as that of the fluid at such a point as B. Since $p_A = 0$, $p_B = V_B - V_A$. Now V_A is equal to that part of V_B which is due to the infinite mass lying below the plane B F. Accordingly the pressure required (p_B) is the potential at B due to the fluid which lies above the plane B F. Thus

$$p_B = \iiint \Pi(f)\,dx\,dy\,dz,$$

where the integrations are to be extended through the region above the plane B F which is external to the sphere B D C E. On the introduction of polar coordinates the integral divides itself into two parts. In the first from $f=0$ to $f=2r$ the spherical shells (*e. g.* D H) are incomplete hemispheres, while in the second part from $f=2r$ to $f=\infty$ the whole hemisphere (*e. g.* I G F) is operative. The spherical area D H, divided by f^2,

$$=2\pi\int_\theta^{\frac{1}{2}\pi}\sin\theta\,d\theta = 2\pi\cos\theta = \pi f/r.$$

The area GF $=2\pi f^2$.

Thus, dropping the suffix B, we get the unexpectedly simple expression

$$p=\frac{\pi}{r}\int_0^{2r}\Pi(f)f^3\,df + 2\pi\int_{2r}^{\infty}\Pi(f)f^2\,df. \quad . \quad . \quad (27)$$

If $2r$ exceed the range of the force, the second integral vanishes and the first may be supposed to extend to infinity. Accordingly

$$p=\frac{\pi}{r}\int_0^{\infty}\Pi(f)f^3\,df = \frac{2}{r}\times\frac{\pi}{8}\int_0^{\infty}f^4\phi(f)\,df, \quad . \quad (28)$$

in accordance with the value (12) already given for T_0. We see then that, if the curvature be not too great, the pressure in the cavity can be calculated as if it were due to a constant tension tending to contract the surface. In the other extreme case where r tends to vanish, we have ultimately

$$p=2\pi\int_0^{\infty}\Pi(f)f^2\,df = K_0.$$

In these extreme cases the results are of course well known; but we may apply (27) to calculate the pressure in the cavity when its diameter is of the order of the range. To illustrate this we may take a case already suggested, in which $\phi(f)=e^{-\beta f}$, $\Pi(f)=\beta^{-1}e^{-\beta f}$. Using these, we obtain on reduction,

$$p=2\pi\beta^{-4}\left\{\frac{3}{\beta r}-e^{-2\beta r}\left(2\beta r+4+\frac{3}{\beta r}\right)\right\}. \quad . \quad . \quad (29)$$

From (29) we may fall back upon particular cases already considered. Thus, if r be very great,

$$p=\frac{2}{r}\times 3\pi\beta^{-5};$$

and if r be very small,

$$p=4\pi\beta^{-4},$$

in agreement with (15).

In a recent memoir* Fuchs investigates a second approximation to the tension of curved surfaces, according to which the pressure in a cavity would consist of two terms; the first (as usual) directly as the curvature, the second subtractive, and proportional to the cube of the curvature. This conclusion does not appear to harmonize with (27), (29), which moreover claim to be exact expressions. It may be remarked that when the tension depends upon the curvature, it can no longer be identified with the work required to generate a unit surface. Indeed the conception of surface-tension appears to be appropriate only when the range is negligible in comparison with the radius of curvature.

The work required to generate a spherical cavity of radius r is of course readily found in any particular case. It is expressed by the integral

$$\int_0^r p\,.\,4\pi r^2.\,dr. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

As a second example we may consider Young's supposition, viz. that the force is unity from 0 to a, and then altogether ceases. In this case by (18), $\Pi(f)$ absolutely vanishes, if $f>a$; so that if the diameter of the cavity at all exceed a, the internal pressure is given rigorously by

$$p=\frac{2}{r}\times\frac{\pi}{8}\int_0^a f^4\phi(f)\,df=\frac{2}{r}\times\frac{\pi a^5}{40}. \quad . \quad . \quad (31)$$

When, on the other hand, $2r<a$, we have

$$p=\frac{\pi}{r}\int_0^{2r}(a-f)f^3\,df+2\pi\int_{2r}^a(a-f)f^2\,df$$

$$=\pi\left\{\frac{a^4}{6}-\frac{4}{3}ar^3+\frac{8}{5}r^4\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

coinciding with (31) when $2r=a$. If $r=0$, we fall back upon $K_0=\pi a^4/6$.

We will now calculate by (30) the work required to form a cavity of radius equal to $\frac{1}{2}a$. We have

$$4\pi\int_0^{\frac{1}{2}a}p\,.\,r^2\,dr=\frac{\pi^2a^7}{4}\left(\frac{1}{18}+\frac{1}{35}\right).$$

The work that would be necessary to form the same cavity,

* *Wien. Ber.* Bd. xcviii. Abth. II. *a*, Mai 1889.

supposing the pressure to follow the law (31) applicable when $2r > a$, is

$$\int_0^{\frac{1}{2}a} \frac{2}{r} \cdot \frac{\pi a^5}{40} \cdot 4\pi r^2\, dr = \frac{\pi^2 a^7}{40}.$$

The work required to generate a cavity for which $2r > a$ is therefore less than if the ultimate law prevailed throughout by the amount

$$\frac{\pi^2 a^7}{4}\left(\frac{1}{10} - \frac{1}{18} - \frac{1}{35}\right) = \frac{\pi^2 a^7}{4 \cdot 9 \cdot 7}. \quad . \quad . \quad . \quad (33)$$

[To be continued.]

XXXV. *On some Problems in the Kinetic Theory of Gases.* *By* S. H. Burbury, *F.R.S.**

Maxwell's *Law of Distribution.*

1. When a gas or mixture of gases is at rest in the normal state, the distribution of velocities among the molecules may be defined thus:—Take an origin O, and let the vector velocity of each molecule be represented by a line drawn from O. Then the number per unit of volume of molecules of mass M, whose velocities are represented by lines from the origin to points within the element of volume dQ at P, is

$$\mathrm{N}\left(\frac{h\mathrm{M}}{\pi}\right)^{\frac{3}{2}} \epsilon^{-h\mathrm{M} \cdot \mathrm{OP}^2}\, d\mathrm{Q}\,;$$

where N is the number of molecules of mass M in unit of volume, and $\frac{3}{2h}$ is the mean kinetic energy of a molecule.

2. I shall employ two other variables :—

Let V denote the vector velocity of the common centre of gravity of two molecules whose masses are M and m. Call this their *common velocity.*

Let R denote the velocity of M, r that of m, relative to this common centre of gravity. Then the velocity of M is the resultant of V and R, that of m is the resultant of V and r.

The relative velocity of M and m is $\mathrm{R}+r$, and shall be denoted by ρ, so that

$$\frac{\mathrm{R}}{r} = \frac{m}{\mathrm{M}}, \quad \rho = \frac{\mathrm{M}+m}{m}\mathrm{R} = \frac{\mathrm{M}+m}{\mathrm{M}}r.$$

3. The molecules whose velocities are represented by lines

* Communicated by the Author.