ON THE THEORY OF SURFACE FORCES.


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 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 aeriform 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

* Méc. Cél. Supplément au Xe livre, 1805:—"Mais il n’a pas tenté, comme Segner, de dériver ces hypothèses, de la loi de l’attraction des molécules, décroissante avec une extrême rapidité; ce qui était indispensable pour les réaliser."

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

* If there be any more volatile impurity (e.g., dissolved gas) ebullition must occur much earlier.
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 \( mm'\phi(f) \), 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

\[
\int_f^\infty \phi(f) \, df = \Pi(f), \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

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

\[
\int_z^\infty \Pi(f) \, df = \psi(z), \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

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 \( \sigma \); (2) the attraction of a particle \( m \) placed at a distance \( z \) from the plane surface of an infinite solid whose density is \( \sigma \)."

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 \( \sigma \), 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

\[
K = 2\pi \sigma^2 \int_0^\infty \psi(z) \, dz. \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]


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

$$K_0 = 2\pi \int_0^\infty \psi (z) \, dz. \quad \ldots \ldots \ldots \ldots (4)$$

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 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 $\sigma_1, \sigma_2$ represent the densities of the two infinite solids, their mutual attraction at distance $z$ is per unit of area

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

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

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

The work required to produce the separation in question is thus

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

and for the tension of a liquid of density $\sigma$ we have

$$T = \pi \sigma^2 \int_0^\infty \theta (z) \, dz. \quad \ldots \ldots \ldots \ldots (8)$$

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

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

* Théorie Mécanique de la Chaleur (Paris, 1869).
Since \( \theta(0) \) is finite, proportional to \( K \), the integrated term vanishes at both limits, and we have simply

\[
\int_0^\infty \theta(z) \, dz = \int_0^\infty z \psi(z) \, dz, \quad \text{.........................(9)}
\]

and

\[
T = \pi \sigma^2 \int_0^\infty z \psi(z) \, dz. \quad \text{.........................(10)}
\]

In Laplace’s notation the second member of (9), multiplied by \( 2\pi \), is represented by \( H \).

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

\[
\int \psi(z) \, dz = z \psi(z) + \frac{1}{2} z^2 \Pi(z) + \frac{1}{3} \int z^2 \phi(z) \, dz,
\]

\[
\int \psi \psi(z) \, dz = \frac{1}{2} z^2 \psi(z) + \frac{1}{3} z^3 \Pi(z) + \frac{1}{4} \int z^4 \phi(z) \, dz.
\]

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

\[
\int_0^\infty \psi(z) \, dz = \frac{1}{2} \int_0^\infty z^2 \phi(z) \, dz, \quad \int_0^\infty \psi \psi(z) \, dz = \frac{1}{3} \int_0^\infty z^4 \phi(z) \, dz; \quad \text{...................(11)}
\]

so that

\[
K = \frac{2\pi}{3} \int_0^\infty z^2 \phi(z) \, dz, \quad T = \frac{\pi}{8} \int_0^\infty z^4 \phi(z) \, dz. \quad \text{.............(12)}
\]

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

\[
\psi (f) = e^{-\delta f}. \quad \text{.........................(13)}
\]

From this we obtain

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

\[
K = 4\pi \delta^{-4}, \quad T = 3\pi \beta^{-6}. \quad \text{.........................(15)}
\]

The range of the attractive force is mathematically infinite, but practically of the order \( \beta^{-1} \), 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 \( \psi(z) = z^n \). From (1), (2), (4) we get

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

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

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

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power. For the transition case, discussed by Sutherland*, of \( n + 4 = 0 \), \( K \) 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.

\[
\phi(z) = \begin{cases} 
1 & \text{from } z = 0 \text{ to } z = a, \\
0 & \text{from } z = a \text{ to } z = \infty;
\end{cases} \tag{17}
\]

and corresponding therewith,

\[
\Pi(z) = a - z \quad \text{from } z = 0 \text{ to } z = a, \\
\Pi(z) = 0 \quad \text{from } z = a \text{ to } z = \infty, \\
\psi(z) = \frac{1}{2}a(a^2 - z^2) - \frac{1}{2}(a^2 - z^2) \quad \text{from } z = 0 \text{ to } z = a, \\
\psi(z) = 0 \quad \text{from } z = a \text{ to } z = \infty. \tag{18, 19}
\]

Equations (12) now give

\[
K = \frac{2\pi}{3} \int_0^\infty z^2dz = \frac{\pi a^4}{6}, \quad T = \frac{\pi}{8} \int_0^a z^4dz = \frac{\pi a^6}{40}. \tag{20, 21}
\]

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 \( T = \frac{\pi}{30}aK \). 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

\[
K = \frac{\pi}{6}(c^4C - r^4R), \quad T = \frac{\pi}{40}(c^4C - r^4R). \tag{22}
\]

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

\[
c^4C = r^4R; \tag{23}
\]

and accordingly

\[
T = \frac{\pi c^4C(c - r)}{40}. \tag{24}
\]

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 formulae 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

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

$f$ 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,

$$p_B - p_A = V_B - V_A.$$  ........................................(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

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

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

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

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.

In the figure \( BDCE \) represents the cavity, and the pressure required is the same as that of the fluid at such a point as \( B \). [\( A \) is supposed to lie upon the external surface.] 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 \( BF \). Accordingly the pressure required \( (p_B) \) is the potential at \( B \) due to the fluid which lies above the plane \( BF \). Thus

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

where the integrations are to be extended through the region above the plane \( BF \) which is external to the sphere \( BDCE \). 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. \( DH \)) are incomplete hemispheres, while in the second part from \( f = 2r \) to \( f = \infty \) the whole hemisphere (e.g. \( IGF \)) is operative. The spherical area \( DH \), divided by \( f^2 \),

\[
= 2\pi \int_0^{\frac{\pi}{2}} \sin \theta \, d\theta = 2\pi \cos \theta = \pi f/r.
\]

The area \( IGF = 2\pi f^2 \).

Thus, dropping the suffix \( B \), we get the unexpectedly simple expression

\[
p = \pi \int_0^{2r} \Pi(f) f^2 \, df + 2\pi \int_{2r}^{\infty} \Pi(f) f^2 \, df, \ldots \ldots (27)
\]

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

\[
p = \frac{\pi}{r} \int_0^{\infty} \Pi(f) f^2 \, df = \frac{2}{r} \times \frac{\pi}{8} \int_0^{\infty} f^4 \phi(f) \, df, \ldots \ldots (28)
\]
in accordance with the value (12) already given for \( T_g \). 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

\[
p = 2\pi \int_0^\infty \Pi (f) f^2 \, df = K_s.
\]

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 \( \phi (f) = e^{-\eta f}, \Pi (f) = \beta^{-1} e^{-\eta f} \). Using these, we obtain on reduction,

\[
p = 2\pi \beta^{-1} \left\{ \frac{3}{\beta r} - e^{-2\beta r} \left( 2\beta r + 4 + \frac{3}{\beta r} \right) \right\}.
\]

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

\[
p = \frac{2}{r} \times 3\pi \beta^{-4};
\]

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

\[
\int_0^r p \cdot 4\pi r^2 \, dr.
\]

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

\[
p = \frac{2}{r} \times \frac{\pi}{8} \int_0^a f^2 \phi (f) \, df = \frac{2}{r} \times \frac{\pi a^6}{40}.
\]

When, on the other hand, \(2r < a\), we have

\[
p = \frac{\pi}{r} \int_0^{2r} (a - f) f^2 \, df + 2\pi \int_0^{a} (a - f) f^2 \, df
\]

\[
= \pi \left\{ \frac{a^4}{6} - \frac{4}{3} ar^3 + \frac{8}{5} r^4 \right\}
\]

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

We will now calculate by (30) the work required to form a cavity of radius equal to \(\frac{1}{4}a\). We have

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

The work that would be necessary to form the same cavity, supposing the pressure to follow the law (31) applicable when \(2r > a\), is

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

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

\[
\frac{\pi^2 a^7}{4} \left( \frac{1}{10} - \frac{1}{18} - \frac{1}{35} \right) = \frac{\pi^2 a^7}{4.97}.
\]

We may apply the same formulae to compare the pressures at the centre and upon the surface of a spherical mass of fluid, surrounded by vacuum. If the radius be \(r\), we have at the centre

\[
V = 4\pi \int_0^r f^2 \Pi (f) \, df;
\]

and at the surface

\[
V = 2\pi \int_0^{2r} \left( 1 - \frac{f}{2r} \right) f^2 \Pi (f) \, df;
\]

so that the excess of pressure at the centre is

\[
4\pi \int_0^r f^2 \Pi (f) \, df - 2\pi \int_0^{2r} f^2 \Pi (f) \, df + \frac{\pi}{r} \int_0^{2r} f^2 \Pi (f) \, df.
\]

If \(r\) exceed the range of the forces, (34) becomes

\[
2\pi \int_0^r f^2 \Pi (f) \, df + \frac{\pi}{r} \int_0^r f^2 \Pi (f) \, df = K + \frac{2T}{r},
\]

as was to be expected. As the curvature increases from zero, there is at first a rise of pressure. A maximum occurs when \(r\) has a particular value, of the order of the range. Afterwards a diminution sets in, and the pressure approaches zero, as \(r\) decreases without limit.

If the surface of fluid, not acted on by external force, be of variable curvature, it cannot remain in equilibrium. For example, at the pole of an oblate ellipsoid of revolution the potential will be greater than at the equator,
so that in order to maintain equilibrium an external polar pressure would be needed. An extreme case is presented by a rectangular mass, in which the potential at an edge is only one half, and at a corner only one \([\text{quarter}]\), of that general over a face.

When the surface is other than spherical, we cannot obtain so simple a general expression as \((34)\) to represent the excess of internal over superficial pressure; but an approximate expression analogous to \((35)\) is readily found.

The potential at a point upon the surface of a convex mass differs from that proper to a plane surface by the potential of the meniscus included between the surface and its tangent plane. The equation of the surface referred to the normal and principal tangents is approximately

\[2z = x^2/R_1 + y^2/R_2,\]

\(R_1, R_2\) being the radii of curvature. The potential, at the origin, of the meniscus is thus

\[V = \int\int \Pi(f) zd\theta,\]

where \(f^2 = x^2 + y^2\); and

\[
\int_0^{2\pi} zd\theta = \int \left(\frac{f^2 \cos^2 \theta}{2R_1} + \frac{f^2 \sin^2 \theta}{2R_2}\right) d\theta = \frac{\pi f^2}{2} \left(\frac{1}{R_1} + \frac{1}{R_2}\right).
\]

Accordingly

\[V = \frac{\pi}{2} \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \int_0^{\pi} f^2 \Pi(f) df = \frac{T}{R_1} + \frac{T}{R_2}.
\]

The excess of internal pressure above that at the superficial point in question is thus

\[K + \frac{T}{R_1} + \frac{T}{R_2}, \quad \text{.................................}(36)\]

in agreement with \((35)\).

For a cylindrical surface of radius \(r\), we have simply

\[K + T/r. \quad \text{.................................}(37)\]

Returning to the case of a plane surface, we know that upon it \(V = K\), and that in the interior \(V = 2K\). At a point \(P\) (Fig. 2) just within the surface, the value of \(V\) cannot be expressed in terms of the principal quantities \(K\) and \(T\), but will depend further upon the precise form of the function \(\Pi\). We can, however, express the value of \(\int V dz\), where \(z\) is measured inwards along the normal, and the integration extends over the whole of the superficial layer where \(V\) differs from \(2K\).

It is not difficult to recognize that this integral must be related to \(T\). For if \(Q\) be a point upon the normal equidistant with \(P\) from the surface \(AB\), the potential at \(Q\) due to
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Fluid below \(AB\) is the same as the potential at \(P\) due to imaginary fluid above \(AB\). To each of these add the potential of the lower fluid at \(P\). Then the sum of the potentials at \(P\) and \(Q\) due to the lower fluid is equal to the potential at \(P\) due to both fluids, that is to the constant \(2K\). The deficiency of potential at a point \(P\) near the plane surface of a fluid, as compared with the potential in the interior, is thus the same as the potential at an external point \(Q\), equidistant from the surface. Now it is evident that \(\int V_0 \, dz\) integrated upwards along the normal represents the work per unit of area that would be required to separate a continuous fluid of unit density along the plane \(AB\) and to remove the parts beyond the sphere of influence, that is, according to the principle of Dupré, \(2T\). We conclude that the deficiency in \(\int V_P \, dz\), integrated along the normal inwards, is also \(2T\); or that

\[
\int_0^z V_P \, dz = 2K \cdot z - 2T, \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (38)
\]

\(z\) being large enough to include the whole of the superficial stratum. The pressure \(p\) at any point \(P\) is given by \(p = V_P - K\), so that

\[
\int_0^z pdz = K \cdot z - 2T, \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (39)
\]

We may thus regard \(2T\) as measuring the total deficiency of pressure in the superficial stratum.

The argument here employed is of course perfectly satisfactory; but it is also instructive to investigate the question directly, without the aid of the idea of superficial tension, or energy, and this is easily done.

In polar coordinates the potential at any point \(P\) is expressed by

\[
V_P = 2\pi \int \int \Pi (f) f^2 \sin \theta d\theta df,
\]

the integrations extending over the whole space \(ACB\) (Fig. 3). If the distance \(EP\), that is \(z\), exceed the range of the forces, every sphere of radius \(f\), under consideration, is complete, and \(V_P = 2K\). But in the integration with respect to \(z\) incomplete spheres have to be considered, such as that shown in the figure. The value of the potential, corresponding to a given infinitely small range of \(f\), is then proportional to

\[
\int_0^\pi \sin \theta d\theta = 1 + \cos \theta = 1 + z/f.
\]

If now we effect first the integration with respect to \(z\), we have as the element of the final integral,

\[
2\pi \Pi (f) f^2 df \left\{ \int_0^f (1 + z/f) \, dz + \int_f^z 2 \, dz \right\},
\]

or

\[
2\pi \Pi (f) f^2 df (2z - \frac{1}{2} f);
\]
and thus, on the whole,

\[ \int_0^z V_p dz = z \cdot 4\pi \int_0^\infty \Pi (f) f^3 df - \pi \int_0^\infty \Pi (f) f^3 df \]

\[ = z \cdot 2K - 2T, \quad \text{as before.} \]

An application of this result to a calculation of the pressure operative between the two halves of an isolated sphere will lead us to another interpretation of \( T \). The pressure in the interior is \( K + 2T/r \), \( r \) being the radius; and this may be regarded as prevailing over the whole of the diametral dividing plane, subject to a correction for the circumferential parts which are near the surface of the fluid. If the radius \( r \) increase without limit, the correction will be the same per unit of length as that investigated for a plane surface. The whole pressure between the two infinite hemispheres is thus

\[ \pi r^2 (K + 2T/r) - 2T \cdot 2\pi r, \quad \text{or} \quad \pi r^2 K - T \cdot 2\pi r. \quad (40) \]

This expression measures equally the attraction between the two hemispheres, which the pressure is evoked to balance. If the fluid on one side of the diametral plane extended to infinity, the attraction upon the other hemisphere, supposed to retain its radius \( r \), would be \( \pi r^2 K \) simply; so that the second term \( T \cdot 2\pi r \) may be considered to represent the deficiency of attraction due to the absence of the fluid external to one hemisphere. Regarding the matter in two dimensions, we recognize \( T \) as the attraction per unit of length perpendicular to the plane of the paper of the fluid occupying (say) the first quadrant \( XOY \) (Fig. 4) upon the fluid in the third quadrant \( X'OY' \), the attraction being resolved in one or other of the directions \( OX, OY \). In its actual direction, bisecting the angle \( XOY \) the attraction will be of course \( \sqrt{2} \cdot T \).

We will now suppose that the sphere is divided by a plane \( AB \) (Fig. 5), which is not diametral, but such that the angle \( BAO = \theta \); \( A0 = r, AB = 2\rho \). In the interior of the mass, and generally along the section \( AB, V = 2K \). On the surface of the sphere, and therefore along the circumference of \( AB, V = K - 2T/r \). When \( V \) was integrated along the normal, from a plane surface inwards, the deficiency was found to be \( 2T \). In the present application the integration is along the oblique line \( AB \), and the deficiency will be \( 2T \sec \theta \). Hence when \( r \) and \( \rho \) increase without limit, we may take as the whole pressure over the area \( AB \)

\[ \pi \rho^2 (K + 2T/r) - 2\pi \rho \cdot 2T \sec \theta = \pi \rho^2 K - 2\pi \rho (2T \sec \theta - T \cos \theta). \]
The deficiency of attraction perpendicular to $AB$ is thus for each unit of perimeter
\[ 2T \sec \theta - T \cos \theta, \]
and this we may think of as applicable in two dimensions (Fig. 6) to each unit of length. When $\theta = 0$, (41) reduces to $T$.

The term $T \cos \theta$ in the expression for the total pressure appears to have its origin in the curvature of the surface, only not disappearing when the curvature vanishes, in consequence of the simultaneous increase without limit of the area over which the pressure is reckoned. If we consider only a distance $AB$, which, though infinite in comparison with the range of the attraction, is infinitely small in comparison with the radius of curvature, $T \cos \theta$ will disappear from the expression for the pressure, though it must necessarily remain in the expression for the attraction. The pressure acting across a section $AB$ proceeding inwards from a plane surface $AE$ of a fluid is thus inadequate to balance the attraction of the two parts. It must be aided by an external force perpendicular to $AB$ of magnitude $T \cos \theta$; and since the imaginary section $AB$ may be made at any angle, we see that the force must be $T$ and must act along $AE$.

An important class of capillary phenomena are concerned with the spreading of one liquid upon the surface of another, a subject investigated experimentally by Marangoni, Van der Mensbrugge, Quincke, and others. The explanation is readily given in terms of surface-tension; and it is sometimes supposed that these phenomena demonstrate in a special manner the reality of surface-tension, and even that they are incapable of explanation upon Laplace's theory, which dealt in the first instance with the capillary pressures due to curvature of surfaces*.

In considering this subject, we have first to express the dependence of the tension at the interface of two bodies in terms of the forces exercised by the bodies upon themselves and upon one another, and to effect this we cannot do better than follow the method of Dupré. If $T_{12}$ denote the interfacial tension, the energy corresponding to unit of area of the interface is also $T_{12}$, as we see by considering the introduction (through a fine tube) of one body into the interior of the other. A comparison with another method of generating the interface, similar to that previously employed when but one body was in question, will now allow us to evaluate $T_{12}$.

The work required to cleave asunder the parts of the first fluid which lie on the two sides of an ideal plane passing through the interior, is per unit

of area $2T_1$, and the free surface produced is two units in area. So for the second fluid the corresponding work is $2T'_2$. This having been effected, let us now suppose that each of the units of area of free surface of fluid (1) is allowed to approach normally a unit of area of (2) until contact is established. In this process work is gained which we may denote by $4T''_{12}$, $2T''_{12}$ for each pair. On the whole, then, the work expended in producing two units of interface is $2T_1 + 2T_2 - 4T''_{12}$, and this, as we have seen, may be equated to $2T_{12}$. Hence

$$T_{12} = T_1 + T_2 - 2T''_{12} ..........................................................(42)$$

If the two bodies are similar, $T_1 = T_2 = T''_{12}$; and $T_{12} = 0$, as it should do.

Laplace does not treat systematically the question of interfacial tension, but he gives incidentally in terms of his quantity $H$ a relation analogous to (42).

If $2T''_{12} > T_1 + T_2$, $T_{12}$ would be negative, so that the interface would of itself tend to increase. In this case the fluids must mix. Conversely, if two fluids mix, it would seem that $T''_{12}$ must exceed the mean of $T_1$ and $T_2$; otherwise work would have to be expended to effect a close alternate stratification of the two bodies, such as we may suppose to constitute a first step in the process of mixture.

The value of $T''_{12}$ has already been calculated (7). We may write

$$T''_{12} = \pi \sigma_1 \sigma_2 \int \theta(z) dz = \frac{1}{3} \pi \sigma_1 \sigma_2 \int \int \phi(z) dz; ............(43)$$

and in general the functions $\theta$ or $\phi$, must be regarded as capable of assuming different forms. Under these circumstances there is no limitation upon the values of the interfacial tensions for three fluids, which we may denote by $T_{12}$, $T_{23}$, $T_{31}$. If the three fluids can remain in contact with one another, the sum of any two of the quantities must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to $T_{12}$, $T_{23}$, $T_{31}$. If the above-mentioned condition be not satisfied, the triangle is imaginary, and the three fluids cannot rest in contact, the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest. For instance, if $T_{31} > T_{12} + T_{23}$, the second fluid spreads itself indefinitely upon the interface of the first and third fluids.

The experimenters who have dealt with this question, Marangoni, Van der Mensbrugghe, Quincke, have all arrived at results inconsistent with the reality of Neumann's triangle. Thus Marangoni says†: "Die gemeinschaft-

† Pogg. Ann. cxxxii. p. 348, 1871 (1865). It was subsequently shown by Quincke that mercury is not really an exception.
liche Oberfläche zweier Flüssigkeiten hat eine geringere Oberflächenspannung als die Differenz der Oberflächenspannung der Flüssigkeiten selbst (mit Ausnahme des Quecksilbers)." Three pure bodies (of which one may be air) cannot accordingly remain in contact. If a drop of oil stands in lenticular form upon a surface of water, it is because the water-surface is already contaminated with a greasy film.

On the theoretical side the question is open until we introduce some limitation upon the generality of the functions. By far the simplest supposition open to us is that the functions are the same in all cases, the attractions differing merely by coefficients analogous to densities in the theory of gravitation. This hypothesis was suggested by Laplace, and may conveniently be named after him. It was also tacitly adopted by Young, in connexion with the still more special hypothesis which Young probably had in view, namely that the force in each case was constant within a limited range, the same in all cases, and vanished outside that range.

As an immediate consequence of this hypothesis we have from (3)

\[ K = K_0 \sigma^2, \quad T = T_0 \sigma^2, \]  

...\(, (44, 45)\)

where \(K_0, T_0\) are the same for all bodies.

But the most interesting results are those which Young* deduced relative to the interfacial tensions of three bodies. By (12), (43),

\[ T_{12} = \sigma_1 \sigma_2 T_0; \]  

...\(, (46)\)

so that by (42), (45),

\[ T_{12} = (\sigma_1 - \sigma_3) T_0. \]  

...\(, (47)\)

According to (47), the interfacial tension between any two bodies is proportional to the square of the difference of their densities. The densities \(\sigma_1, \sigma_2, \sigma_3\) being in descending order of magnitude, we may write

\[ T_{13} = (\sigma_1 - \sigma_2 + \sigma_2 - \sigma_3) T_0 = T_{12} + T_{23} + 2 (\sigma_1 - \sigma_2) (\sigma_2 - \sigma_3) T_0; \]

so that \(T_{23}\) necessarily exceeds the sum of the other two interfacial tensions. We are thus led to the important conclusion, so far as I am aware hitherto unnoticed, that according to this hypothesis Neumann's triangle is necessarily imaginary, that one of three fluids will always spread upon the interface of the other two.

Another point of importance may be easily illustrated by this theory, viz. the dependency of capillarity upon abruptness of transition. "The reason why the capillary force should disappear when the transition between two liquids is sufficiently gradual will now be evident. Suppose that the transition from 0 to \(\sigma\) is made in two equal steps, the thickness of the intermediate layer of density \(\frac{1}{2} \sigma\) being large compared to the range of the molecular forces, but small in comparison with the radius of curvature. At

each step the difference of capillary pressure is only one quarter of that due to the sudden transition from 0 to $\sigma$, and thus altogether half the effect is lost by the interposition of the layer. If there were three equal steps, the effect would be reduced to one third, and so on. When the number of steps is infinite, the capillary pressure disappears altogether.*

According to Laplace's hypothesis the whole energy of any number of contiguous strata of liquids is least when they are arranged in order of density, so that this is the disposition favoured by the attractive forces. The problem is to make the sum of the interfacial tensions a minimum, each tension being proportional to the square of the difference of densities of the two contiguous liquids in question. If the order of stratification differ from that of densities, we can show that each step of approximation to this order lowers the sum of tensions. To this end consider the effect of the abolition of a stratum $\sigma_{n+1}$, contiguous to $\sigma_n$ and $\sigma_{n+2}$. Before the change we have

$$(\sigma_n - \sigma_{n+1})^2 + (\sigma_{n+1} - \sigma_{n+2})^2,$$

and afterwards $(\sigma_n - \sigma_{n+2})^2$. The second minus the first, or the increase in the sum of tensions, is thus

$$2(\sigma_n - \sigma_{n+1})(\sigma_n - \sigma_{n+2}).$$

Hence, if $\sigma_{n+1}$ be intermediate in magnitude between $\sigma_n$ and $\sigma_{n+2}$, the sum of tensions is increased by the abolition of the stratum; but, if $\sigma_{n+1}$ be not intermediate, the sum is decreased. We see, then, that the removal of a stratum from between neighbours where it is out of order and its introduction between neighbours where it will be in order is doubly favourable to the reduction of the sum of tensions; and since by a succession of such steps we may arrive at the order of magnitude throughout, we conclude that this is the disposition of minimum tensions and energy.

So far the results of Laplace's hypothesis are in marked accordance with experiment; but if we follow it out further, discordances begin to manifest themselves. According to (47)

$$\sqrt{T_{13}} = \sqrt{T_{12}} + \sqrt{T_{21}}, \text{ ..................................(48)}$$

a relation not verified by experiment. What is more, (47) shows that according to the hypothesis $T_{12}$ is necessarily positive; so that, if the preceding argument be correct, no such thing as mixture of two liquids could ever take place.

But although this hypothesis is clearly too narrow for the facts, it may be conveniently employed in illustration of the general theory. In extension of (25) the potential at any point may be written

$$V = \int \int \int \sigma \Pi (f) \, dx \, dy \, dz, \text{ ..................................(49)}$$

and the hydrostatical equation of equilibrium is

$$dp = \sigma \, dV. \text{ ..............................................(50)}$$

By means of the potential we may prove, independently of the idea of surface tension, that three fluids cannot rest in contact. Along the surface of contact of any two fluids the potential must be constant. Otherwise, there would be a tendency to circulation round a circuit of which the principal parts are close and parallel to the surface, but on opposite sides. For in the limit the variation of potential will be equal and opposite in the two parts of the circuit, and the resulting forces at corresponding points, being proportional also to the densities, will not balance. It is thus necessary to equilibrium that there be no force at any point; that is, that the potential be constant along the whole interface.

It follows from this that if three fluids can rest in contact, the potential must have the same constant value on all the three intersecting interfaces. But this is clearly impossible, the potential on each being proportional to the sum of the densities of the two contiguous fluids, as we see by considering places sufficiently removed from the point of intersection.

According to Laplace's hypothesis, then, three fluids cannot rest in contact; but the case is altered if one of the bodies be solid. It is necessary, however, that the quality of solidity attach to the body of intermediate density. For suppose, for example (Fig. 9), that the body of greatest density, \( \sigma_1 \), is solid, and that fluids of densities \( \sigma_2, \sigma_3 \) touch it and one another. It is now no longer necessary that the potential be constant along the interfaces (1, 2), (1, 3); but only along the interface (3, 2). The potential at a distant point of this interface may be represented by \( \sigma_1 + \sigma_2 \). But at the point of intersection the potential cannot be so low as this, being at least equal to \( \sigma_1 + \sigma_3 \), even if the angle formed by the two faces of (2) be evanescent. By this and similar reasoning it follows that the conditions of equilibrium cannot be satisfied, unless the solid be the body of intermediate density \( \sigma_2 \).

One case where equilibrium is possible admits of very simple treatment. It occurs when \( \sigma_2 = \frac{1}{2}(\sigma_1 + \sigma_3) \), and the conditions are satisfied by supposing (Fig. 10) that the fluid interface is plane and perpendicular to the solid wall. At a distance from \( O \) the potential is represented by \( \sigma_1 + \sigma_3 \); and the same value obtains at a point \( P \), near \( O \), where the sphere of influence cuts into (2). For the areas of spherical surface lost by (1) and (3) are equal, and are replaced by equal areas of (2); so that if the above condition between the densities holds good, the potential is constant all the way up to \( O \). The sub-case, where \( \sigma_2 = 0, \sigma_3 = \frac{1}{2}\sigma_1 \), was given by Clairaut.
If the intermediate density differ from the mean of the other two, the problem is less simple; but the general tendency is easily recognized. If, for example, \( \sigma_2 > \frac{1}{2} (\sigma_1 + \sigma_3) \), it is evident that along a perpendicular interface the potential would increase as \( O \) is approached. To compensate this the interface must be inclined, so that, as \( O \) is approached, \( \sigma_1 \) loses its importance relatively to \( \sigma_2 \). In this case therefore the angle between the two faces of (1) must be acute.

The general problem was treated by Young by means of superficial tensions, which must balance when resolved parallel to the surface of the solid, though not in the perpendicular direction. In this way Young found at once

\[ T_\| \cos \theta + T_\perp = T_m; \]

or rather, in terms of the more special hypothesis,

\[ (\sigma_1 - \sigma_3)^2 \cos \theta + (\sigma_1 - \sigma_2)^2 = (\sigma_2 - \sigma_3)^2. \]

From this we deduce

\[ \cos \theta = \frac{2\sigma_3 - \sigma_1 - \sigma_2}{\sigma_2 - \sigma_3}, \]

in agreement with what we found above for a special case. The equation may also be written

\[ \sigma_1 \cos^2 \frac{1}{2} \theta + \sigma_2 \sin^3 \frac{1}{2} \theta = \sigma_3; \]

or if, as we may suppose without real loss of generality, \( \sigma_3 = 0 \),

\[ \sigma_1 \cos^2 \frac{1}{2} \theta = \sigma_2. \]

a form given by Laplace. In discussing the equation (53) with \( \sigma_3 = 0 \), Young* remarks:—"Supposing the attractive density of the solid to be very small, the cosine will approach to \(-1\), and the angle of the liquid to two right angles; and on the other hand, when \( \sigma_2 \) becomes equal to \( \sigma_1 \), the cosine will be \(1\), and the angle will be evanescent, the surface of the liquid coinciding in direction with that of the solid. If the density \( \sigma_2 \) be still further increased, the angle cannot undergo any further alteration, and the excess of force will only tend to spread the liquid more rapidly on the solid, so that a thin film would always be found upon its surface, unless it were removed by evaporation, or unless its formation were prevented by some unknown circumstance which seems to lessen the intimate nature of the contact of liquids with solids."

The calculation of the angle of contact upon these lines is thus exceedingly simple, but I must admit that I find some difficulty in forming a definite conception of superficial tension as applied to the interface of a solid and a fluid. It would seem that interfacial tension can only be employed in


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such cases as the immediate representative of interfacial energy, as conceived by Gauss. This principle, applied to a hypothetical displacement in which the point of meeting travels along the wall, leads with rigour to the required result.

In view of the difficulties which have been felt upon this subject, it seems desirable to show that the calculation of the angle of contact can be made without recourse to the principle of interfacial tension or energy. This indeed was effected by Laplace himself, but his process is very circuitous. Let \( OP M \) be the surface of fluid \((\sigma_1)\) resting against a solid wall \( ON \) of density \( \sigma_2 \). Suppose also that \( \sigma_2 = 0 \), and that there is no external pressure on \( OM \). At a point \( M \) at a sufficient distance from \( O \) the curvature must be uniform (or the potential could not be constant), and we will suppose it to be zero. It would be a mistake, however, to think that the surface can be straight throughout up to \( O \). This we may recognize by consideration of the potential at a point \( P \) just near enough to \( O \) for the sphere of influence to cut the solid. As soon as this occurs, the potential would begin to vary by substitution of \( \sigma_2 \) for \( \sigma_1 \), and equilibrium would fail. The argument does not apply if \( \theta = \frac{1}{2} \pi \).

We may attain the object in view by considering the equilibrium of the fluid \( MNO \), or rather of the forces which tend to move it parallel to \( ON \). Of pressures we have only to consider that which acts across \( MN \), for on \( OM \) there is no pressure, and that on \( ON \) has no component in the direction considered. Moreover, the solid \( \sigma_2 \) below \( ON \) exercises no attraction parallel to \( ON \). Equilibrium therefore demands that the pressure operative across \( MN \) shall balance the horizontal attraction exercised upon \( OMN \) by the fluid \( \sigma_1 \) which lies to the right of \( MN \). The evaluation of the attraction in such cases has been already treated. It is represented by \( MN. \sigma_1^2 K_\theta \), subject to corrections for the ends at \( M \) and \( N \). The correction for \( M \) we have seen to be \( \sigma_2^2 T_\theta (2 \sec \theta - \cos \theta) \), and for \( N \) it is \( \sigma_1^2 T_\theta \). On the whole the attraction in question is therefore

\[
\sigma_2^2 [MN. K_\theta - 2T_\theta \sec \theta + T_\theta \cos \theta - T_\theta].
\]

We have next to consider the pressure. In the interior of \( MN \), we have \( \sigma_2^2 K_\theta \); but the whole pressure \( MN. \sigma_2^2 K_\theta \) is subject to corrections for the ends. The correction for \( M \) we have seen to be \( 2\sigma_2^2 T_\theta \sec \theta \). In the neighbourhood of \( N \) the potential, and therefore the pressure, is influenced by the solid. If \( \sigma_2 \) were zero, the deficiency would be \( 2\sigma_1^2 T_\theta \). If \( \sigma_2 \) were equal to \( \sigma_1 \), there would be no deficiency. Under the actual circumstances the deficiency is accordingly

\[
2\sigma_1 (\sigma_1 - \sigma_2) T_\theta;
\]
so that the expression for the total pressure operative across $MN$ is

$$\sigma_1 [MN, \sigma_1 k + 2\sigma_1 T \sec \theta - 2(\sigma_1 - \sigma_2) T].$$

If we now equate the expressions for the pressure and the resolved attraction, we find as before

$$\sigma_1 (1 - \cos \theta) = 2 (\sigma_1 - \sigma_2).$$

In connexion with edge-angles it may be well here to refer to a problem, which has been the occasion of much difference of opinion—that of the superposition of several liquids in a capillary tube. Laplace’s investigation led him to the conclusion that the whole weight of liquid raised depends only upon the properties of the lowest liquid. Thereupon Young* remarks:—

"This effect may be experimentally illustrated by introducing a minute quantity of oil on the surface of the water contained in a capillary tube, the joint elevation, instead of being increased as it ought to be according to Mr Laplace, is very conspicuously diminished; and it is obvious that since the capillary powers are represented by the squares of the density of oil and of its difference from that of water, their sum must be less than the capillary power of water, which is proportional to the square of the sum of the separate quantities."

But the question is not to be dismissed so summarily. That Laplace’s conclusion is sound, upon the supposition that none of the liquids wets the walls of the tube, may be shown without difficulty by the method of energy. In a hypothetical displacement the work done against gravity will balance the work of the capillary forces. Now it is evident that the liquids, other than the lowest, contribute nothing to the latter, since the relation of each liquid to its neighbours and to the walls of the tube is unaltered by the displacement. The only effect of the rise is that a length of the tube before in contact with air is replaced by an equal length in contact with the lowest liquid. The work of the capillary forces is the same as if the upper liquids did not exist, and therefore the total weight of the column supported is independent of these liquids.

The case of Young’s experiment, in which oil stands upon water in a glass tube, is not covered by the foregoing reasoning. The oil must be supposed to wet the glass, that is to insinuate itself between the glass and air, so that the upper part of the tube is covered to a great height with a very thin layer of oil. The displacement here takes place under conditions very different from before. As the column rises, no new surface of glass is touched by oil, while below water replaces oil. The properties of the oil are thus brought into play, and Laplace’s theorem does not apply.

That theory indicates the almost indefinite rise of a liquid like oil in contact with a vertical wall of glass is often overlooked, in spite of Young's explicit statement quoted above. It may be of interest to look into the question more narrowly on the basis of Laplace's hypothesis.

If we include gravity in our calculations, the hydrostatic equation of equilibrium is

\[ p = \text{const.} + \sigma V - gpz, \] ........................(56)

where \( z \) is measured upwards, and \( V \) denotes as before the potential of the cohesive forces. Along the free surface of the liquid the pressure is constant, so that

\[ \sigma V = \sigma^2 K_s + gpz, \] ..............................(57)

\( z \) being reckoned from a place where the liquid is deep and the surface plane.

At a point upon the surface, whose distance from the wall exceeds the range of the forces,

\[ \sigma V = K + T \left( \frac{1}{R_1} + \frac{1}{R_2} \right); \] ..............................(58)

or, if we take the problem in two dimensions,

\[ \sigma V = K + T/R, \] ..............................(59)

where \( R \) is the radius of curvature, and \( K, T \) denote the intrinsic pressure and tension proper to the liquid and proportional to \( \sigma^2 \). Upon this equation is founded the usual calculation of the form of the surface.

When the point under consideration is nearer to the wall than the range of the forces, the above expression no longer applies. The variation of \( V \) on the surface of the thin layer which rises above the meniscus is due not to variations of curvature, for the curvature is here practically evanescent, but to the inclusion within the sphere of influence of the more dense matter constituting the wall. If the attraction be a simple function of the distance, such as those considered above in illustrative examples, the thickness of the layer diminishes constantly with increasing height. The limit is reached when the thickness vanishes, and the potential attains the value due simply to the solid wall. This potential is \( \sigma K_s \), the intrinsic pressure within the wall being \( \sigma^2 K_s \); so that if we compare the point above where the layer of fluid disappears with a point below upon the horizontal surface, we find

\[ gpz = \sigma (\sigma' - \sigma) K_s. \] ..............................(60)

By this equation is given the total head of liquid in contact with the wall; and, as was to be expected, it is enormous.

The height of the meniscus itself in a very narrow tube wetted by the liquid is obtained from (57), (58). If \( R \) be the radius of curvature at the centre of the meniscus,

\[ gpz = 2T/R; \] ..............................(61)
and $R$ may be identified with the radius of the tube, for under the circumstances supposed the meniscus is very approximately hemispherical.

The calculation of the height by the method of energy requires a little attention. The simplest displacement is an equal movement upwards of the whole body of liquid, including the layer above the meniscus. In this case the work of the cohesive forces depends upon the substitution of liquid for air in contact with the tube, and therefore not merely upon the interfacial tension between liquid and air, as (61) might lead us to suppose. The fact is that in this way of regarding the subject the work which compensates that of the cohesive forces is not simply the elevation against gravity of the column ($z$), but also an equal elevation of the very high, though very thin, layer situated above it. The complication thus arising may be avoided by taking the hypothetical displacement so that the thin layer does not accompany the column ($z$). In this case the work of the cohesive forces depends upon a reduction of surface between liquid and air simply, without reference to the properties of the walls, and (61) follows immediately.

Laplace’s integral $K$ was, as we have seen, introduced originally to express the intrinsic pressure, but according to the discovery of Dupré* it is susceptible of another and very important interpretation. "Le travail de désagrégation totale d’un kilogramme d’un corps quelconque égale le produit de l’attraction au contact par le volume, ou, ce qui équivaut, le travail de désagrégation totale de l’unité de volume égale l’attraction au contact.” *Théorie Mécanique de la Chaleur, 1869, p. 152.

Attraction au contact here means what we have called intrinsic pressure. The following reasoning is substantially that of Dupré.

We have seen (2) that $2\pi m\sigma \psi (z)$ represents the attraction of a particle $m$ placed at distance $z$ from the plane surface of an infinite solid whose density is $\sigma$. The work required to carry $m$ from $z = 0$ to $z = \infty$ is therefore

$$2\pi m\sigma \int_0^\infty \psi (z) dz = m\sigma K_0,$$

by (4); so that the work necessary to separate a superficial layer of thickness $dz$ from the rest of the mass and to carry it beyond the range of the attraction is $\sigma^2 dz K_0$. The complete disaggregation of unit of volume into infinitesimal slices demands accordingly an amount of work represented by $\sigma^2 K_0$, or $K$. The work required further to separate the infinitesimal slices into component filaments or particles and to remove them beyond the range of the mutual attraction is negligible in the limit, so that $K$ is the total work of complete disaggregation.

A second law formulated by Dupré is more difficult to accept. "Pour un même corps prenant des volumes variés, le travail de désagrégation restant

* Van der Waals gives the same result in his celebrated essay of 1873.—German Translation, 1881, p. 81.
à accomplir est proportionel à la densité ou en raison inverse du volume.”
The argument is that the work remaining to be done upon a given mass at any stage of the expansion is proportional first to the square of the density, and secondly to the actual volume, on the whole therefore inversely as the volume. The criticism that I am inclined to make here is that Dupré's theory attempts either too little or too much. If we keep strictly within the lines of Laplace's theory the question here discussed cannot arise, because the body is supposed to be incompressible. That bodies are in fact compressible may be so much the worse for Laplace's theory, but I apprehend that the defect cannot be remedied without a more extensive modification than Dupré attempts. In particular, it would be necessary to take into account the work of compression. We cannot leave the attractive forces unbalanced; and the work of the repulsive forces can only be neglected upon the hypothesis that the compressibility itself is negligible. Indeed it seems to me, that a large part of Dupré's work, important and suggestive as it is, is open to a fundamental objection. He makes free use of the two laws of thermodynamics, and at the same time rests upon a molecular theory which is too narrow to hold them. One is driven to ask what is the real nature of this heat, of which we hear so much. It seems hopeless to combine thermodynamics with a merely statical view of the constitution of matter.

On these grounds I find it difficult to attach a meaning to such a theorem as that enunciated in the following terms* ：“La dérivée partielle du travail mécanique interne prise par rapport au volume égale l'attraction par mètre carré qu'exercent l'une sur l'autre les deux parties du corps situées des deux côtés d'une section plane,” viz. the intrinsic pressure. In the partial differentiation the volume is supposed to vary and the temperature is supposed to remain constant. The difficulty of the first part of the supposition has been already touched upon; and how in a fundamental theory can we suppose temperature to be constant without knowing what it is? It is possible, however, that some of these theorems may be capable of an interpretation which shall roughly fit the facts, and it is worthy of consideration how far they may be regarded as applicable to matter in a state of extreme cold.

With respect to the value of $K$, Young's estimate of 23,000 atmospheres for water has already been referred to. It is not clear upon what basis he proceeded, but a chance remark suggests that it may have been upon the assumption that cohesion was of the same order of magnitude in liquids and solids. Against this, however, it may be objected that the estimate is unduly high. Even steel is scarcely capable of withstanding a tension of 23,000 atmospheres.

* Loc. cit. p. 47.
So far as I am aware, the next estimates of $K$ are those of Dupré. One of them proceeds upon the assumption that for rough purposes $K$ may be identified with the mechanical equivalent of the heat rendered latent in the evaporation of the liquid, that in fact evaporation may be regarded as a process of disaggregation in which the cohesive forces have to be overcome. This view appears to be substantially sound. If we take the latent heat of water as 600°, we find for the work required to disintegrate one gram of water

$$600 \times 4.2 \times 10^7$$ C.G.S.

One atmosphere is about 10⁶ C.G.S.; so that

$$K = 25,000$$ atmospheres.

The estimates of his predecessors were apparently unknown to Van der Waals, who (in 1873) undertook his work mainly with the object of determining the quantity in question. He finds for water 11,000 atmospheres. The application of Clausius's equation of virial to gases and liquids is obviously of great importance; but, as it lies outside the scope of the present paper, I must content myself with referring the reader to the original memoir and to the account of it by Maxwell*.

One of the most remarkable features of Young's treatise is his estimate of the range $a$ of the attractive force on the basis of the relation $T = \frac{1}{3} a K$. Never once have I seen it alluded to; and it is, I believe, generally supposed that the first attempt of the kind is not more than twenty years old. Estimating $K$ at 23,000 atmospheres, and $T$ at 3 grains per inch, Young finds† that "the extent of the cohesive force must be limited to about the 250 millionth of an inch"; and he continues, "nor is it very probable that any error in the suppositions adopted can possibly have so far invalidated this result as to have made it very many times greater or less than the truth." It detracts nothing from the merit of this wonderful speculation that a more precise calculation does not verify the numerical coefficient in Young's equation. The point is that the range of the cohesive force is necessarily of the order $T/K$.

But this is not all. Young continues:—"Within similar limits of uncertainty, we may obtain something like a conjectural estimate of the mutual distance of the particles of vapours, and even of the actual magnitude of the elementary atoms of liquids, as supposed to be nearly in contact with each other; for if the distance at which the force of cohesion begins is constant at the same temperature, and if the particles of steam are condensed when they approach within this distance, it follows that at 60° of Fahrenheit the distance of the particles of pure aqueous vapour is about the 250 millionth of an inch;
and since the density of this vapour is about one sixty thousandth of that of water, the distance of the particles must be about forty times as great; consequently the mutual distance of the particles of water must be about the ten thousand millionth of an inch. It is true that the result of this calculation will differ considerably according to the temperature of the substances compared.... This discordance does not, however, wholly invalidate the general tenour of the conclusion...and on the whole it appears tolerably safe to conclude that, whatever errors may have affected the determination, the diameter or distance of the particles of water is between the two thousand and the ten thousand millionth of an inch." This passage, in spite of its great interest, has been so completely overlooked that I have ventured briefly to quote it, although the question of the size of atoms lies outside the scope of the present paper.

Another matter of great importance to capillary theory I will only venture to touch upon. When oil spreads upon water, the layer formed is excessively thin, about two millionths of a millimetre. If the layer be at first thicker, it exhibits instability, becoming perforated with holes. These gradually enlarge, until at last, after a series of curious transformations, the superfluous oil is collected in small lenses. It would seem therefore that the energy is less when the water is covered by a very thin layer of oil, than when the layer is thicker. Phenomena of this kind present many complications, for which various causes may be suggested, such as solubility, volatility, and—perhaps more important still—chemical heterogeneity. It is at present, I think, premature to draw definite physical conclusions; but we may at least consider what is implied in the preference for a thin as compared with a thicker film.

The passage from the first stage to the second may be accomplished in the manner indicated in Figs. 13, 14, 15. We begin (Fig. 13) with a thin layer of oil on water and an independent thick layer of oil. In the second stage (Fig. 14) the thick layer is split in two, also thick in comparison with the range of the cohesive forces, and the two parts are separated. In the third stage one of the component layers is brought down until it coalesces with the thin layer on water. The last state differs from the first by the
substitution of a thick film of oil for a thin one in contact with the water, and we have to consider the work spent or gained in producing the change. If, as observation suggests, the last state has more energy than the first, it follows that more work is spent in splitting the thick layer of oil than is gained in the approach of a thick layer to the already oiled water. At some distances therefore, and those not the smallest, oil must be more attracted (or less repelled) by oil than by water. The reader will not fail to notice the connexion between this subject and the black of soap-films investigated by Profs. Reinold and Rücker [Phil. Trans. 172, p. 645, 1884].

[1901. Continuations of the present memoir under the same title will be found below, reprinted from Phil. Mag. xxxiii. pp. 209, 468, 1892. Reference may be made also to Phil. Mag. xlviii. p. 331, 1899.]